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ON THE REACTIONS OF BOTH THE IONS AND THE NONIONIZED FORMS OF ELECTROLYTES [1]

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[FIFTEENTH[2] COMMUNICATION ON CATALYSIS]

(We are indebted to the Carnegie Institution of Washington for aid in these researches.)

After Arrhenius[3] brought out his theory of the electrolytic dissociation of electrolytes, and Ostwald[4] and Arrhenius and their students found a fairly close agreement between the "strength" of an acid or a base as determined by the conductivity method and by the velocity of the hydrolysis of cane sugar, acetamide, and methyl or ethyl acetate, the opinion gradually grew that electrolytes react through the ionized portions exclusively. In fact, although it was known that *nonionizable* (in the ordinary sense!) substances, such as trialkylamines and alkyl halides, react readily, and the Arrhenius

[1] A lecture delivered before the Chemistry Department of Princeton University on Mar. 7, 1913.

[2] THIS JOURNAL, **27**, 118; **28**, 370; **31**, 185; **32**, 606; **37**, 71, 361; **38**, 1, 258, 489, 746; **39**, 124, 145, 226, 300; **41**, 457, 483; **42**, 115; **43**, 358, 505; **44**, 219; **48**, 352; **49**, 116. Ber. d. chem. Ges., **33**, 1520; **35**, 553; **36**, 3139; **37**, 184, 618; **41**, 3199. Science, **30**, 617 (1909). J. Am. Chem. Soc., **30**, 1755.

[3] Z. physik. Chem., **1**, 631.

[4] J. prakt. Chem., [2] **27**, 1; **28**, 449; **29**, 406; **30**, 231; **31**, 307; **33**, 352; **35**, 112. Z. physik. Chem., **2**, 36, 136, 270.

[5] *Ibid.*, **1**, 110; **2**, 284; **4**, 226; **28**, 217, 326.

theory was criticized by many, especially Kahlenberg[1] and Michael,[2] the theory that all chemical reactions are purely ionic was the one generally accepted up to within the last few years. This belief was probably strengthened greatly by the discovery of the role of simple and complex ions in the electrochemical phenomena so successfully studied in the development of Nernst's[3] theory, and the simple relation existing between the concentration of the ions and the magnitude of the electromotive force observed when a metallic (or gaseous) electrode is immersed in a solution of its ions.

Even in the application of physical chemical conceptions to the study of organic reactions, the very field where the purely ionic theory should have found soil least adapted to its unopposed growth, some of the best workers, Goldschmidt,[4] Bredig,[5] Lapworth,[6] Wegscheider,[7] and Stieglitz,[8] as late as 1908, *did not* apply the conception that *besides* the simple or complex organic ions the *nonionized* portions of the *electrolytes* formed from them are concerned in all catalytic phenomena of organic chemistry in which acids, bases or salts react. However, this new conception of the activity of *nonionized electrolytes* must not be confounded with that involving the activity of *nonelectrolytes*. Thus Stieglitz proved in 1903 that *nonionizable* aminophenyl esters rearrange, acids retarding the reaction catalytically through salt formation, and in particular he proved in 1905 (Dissertation of Schlesinger, Univ. of Chicago) that the nonionized molecules of imido esters decompose in aqueous solutions with characteristic velocity differing most decidedly from the coefficient for their *anions*. But in nearly all of these examples, and others which we have discussed in

[1] J. Phys. Chem., **5**, 339 (1901); **6**, 1 (1902), and subsequent papers in the same journal.

[2] This Journal, **43**, 322.

[3] Z. physik. Chem., **2**, 613; **4**, 129. Wied. Ann., **45**, 360. Nernst's Theoretische Chemie, **1907**, p. 729.

[4] Z. Elektrochem., **15**, 6. Z. physik. Chem., **60**, 728; **70**, 627. Ber. d. chem. Ges., **39**, 711.

[5] Z. Elektrochem., **9**, 118; **10**, 586; **11**, 528; **15**, 535, 539.

[6] J. Chem. Soc., **79**, 1269; **81**, 1503 and 1512; **85**, 31; **91**, 1133; **93**, 30, 85, 2165, 2187. Chem. News, **97**, 248, 309 and 310.

[7] Z. physik. Chem., **39**, 257; **41**, 62, and later articles.

[8] This Journal, **39**, 29, 166, 402, 437, 586, 719. J. Am. Chem. Soc., **33**, 221; **34**, 1687.

various articles, the reactions are due to the activity of *non-electrolytes* and these cases are therefore entirely different from the ones involving *nonionized electrolytes* that we are considering in this paper.

After all it is not difficult to understand in these days of electrons that neutral molecules of either *electrolytes* or *non-electrolytes* can react like the ions. The brilliant ideas of J. J. Thomson[1] and his postulation of "electrostatic induction"[2]

Fig I

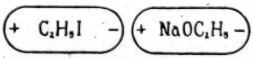

Fig II

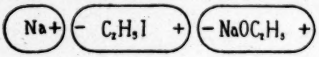

Fig III.

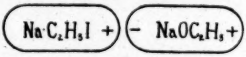

Fig IV.

may aid us greatly in the study of such reactions. If, in Fig. I, the negative ethylate ion influences a neighboring molecule of ethyl iodide by "electrostatic induction," the particles making up the ethyl iodide molecule must become a "doublet" and rearrange in such a way that the portion nearer the ethylate ion becomes, *in effect*, positive, and therefore capable of attracting the negative ethylate ion as a pith ball is attracted to a charged body. When the ethylate ion and ethyl iodide are drawn together electrically the resulting complex ion can decompose into an iodide ion and ethyl ether.

Now neutral molecules may *at intervals* combine in the same way. A number of colleagues in physics have agreed that through collision or other mechanical disturbance the atomic particles and electrons of the ethyl iodide and sodium ethylate in Fig. II may be so disarranged that a portion of one molecule may become, *in effect*, positive and another portion negative. If the neighboring portions of the two molecules differ elec-

[1] For references to the literature see J. J. Thomson: "The Corpuscular Theory of Matter," pp. 120–141 (1907). L. G. Winston: THIS JOURNAL, **45**, 547. Acree: *Ibid.*, **45**, 372.

[2] Thomson: *Loc. cit.*, p. 135. Winston: *Loc cit.*

trically, the molecules will be drawn together into a complex structure which can then decompose into sodium iodide and ethyl ether. If the neighboring portions of the two molecules are alike electrically they will be repelled for the moment, to combine afterwards when the conditions are favorable.

Different compounds may vary in the readiness with which they assume the condition favorable for reaction, and hence react with different velocities.

The same ideas may explain to a certain extent the peculiar effect which added salts have on some reactions. The sodium ion in Fig. III may by "induction" charge the ethyl iodide as illustrated, and the sodium ethylate may in turn be influenced by the adjacent positive portion of the ethyl iodide. The ethyl iodide and sodium ethylate therefore attract each other, combine, and then decompose into sodium iodide and ethyl ether. It may well be that many cases of catalysis by acids, bases and salts depend upon this "action at a distance" by the ions, instead of an actual combination illustrated in Fig. IV. We see that it is possible for the sodium ion and ethyl iodide of Fig. III to combine and give the complex cation, sodium-ethyl iodide, illustrated in Fig. IV. This complex cation could then *induce* charges in the sodium ethylate, as illustrated, combine with it and form a complex sodium-sodium ethylate-ethyl iodide compound which decomposes into a sodium ion, sodium iodide and ethyl ether. A negative catalysis would result when the catalyzing ion interferes with the tendency of one of the substances to assume a form favorable for action. To give one of many illustrations, this could happen if the sodium ion attracts toward it, or to it, that portion of the ethyl iodide, for example, which must be adjacent to the sodium ethylate before reaction can proceed.

Many of these changes could be as well explained on Thomson's ideas of "electronic pressure" and the *transfer of electrons* before the actual combination and reaction.

When Brunel and Acree began work in 1905 on the theory that *both the ions and the nonionized molecules must be considered in all reactions of electrolytes* there was already some

evidence from the older work of Arrhenius, Ostwald, Blanksma,[1] van Dam[2] and others that the ***nonionized electrolytes*** are active in many chemical reactions. In the very tables that Ostwald published to prove the *same activity* of the hydrogen ions of acids in conductivities and in the hydrolysis of cane sugar, methyl acetate, and acetamide, there were many discrepancies larger than experimental errors that caused us to believe that the nonionized acids (and bases) are also concerned in these chemical reactions. The following table[3] shows some cases in which the *activity* of the hydrogen ions is apparently considerably larger in the hydrolysis of methyl acetate and cane sugar than in the conduction of electrons.

Name of acid	Conductivity[4]	Hydrolysis of methyl acetate	Hydrolysis of cane sugar
Acetylformic acid, $CH_3COCOOH$	5.60	6.70	6.49
Trichloroacetic acid, CCl_3COOH	62.3	68.2	75.4
Benzenesulphonic acid, $C_6H_5SO_3H$	74.8	99.0	104.0
Isothionic acid, $C_2H_4(OH)SO_3H$	77.8	98.0	92.0
Ethylsulphonic acid, $C_2H_5SO_3H$	79.9	98.0	91.0
Sulphuric acid, H_2SO_4	65.1	73.9	73.2

All of these examples, and others in which the second and third columns are smaller than the first one, could be interpreted on the basis that ***the nonionized acids also show an activity in these chemical reactions.*** The greater magnitude of the numbers in Columns 3 and 4, as contrasted with those in Column 2, shows the apparent activity of the nonionized acids (or both ions together), this activity being greater in the hydrolysis of methyl acetate in some cases, but greater in the inversion of cane sugar in other examples, as was predicted from our theory. The trouble with most of this earlier work was

[1] Rec. trav. chim., **21**, 366; **22**, 290.

[2] *Ibid.*, **18**, 408; **19**, 318.

[3] Ostwald's Lehrbuch, **2**, 1, 650. J. prakt. Chem., [2] **30**, 95.

[4] In all of his earlier work Ostwald calculated the per cent. of ionization on the assumption that the value for μ_∞ is the same for all acids (Z. physik. Chem., **1**, 78).

that only one concentration of the catalyzing acid had been used, and we did not have sufficient very accurate data on the varying concentrations and reaction velocities, and the varying degrees of ionization of the catalyzing acids, to allow us to determine accurately to what extent *both the hydrogen ions and the nonionized acids are catalytically active.* In a few cases, however, the concentration of the acid was varied considerably and Arrhenius[1] and Ostwald[2] recognized from the latter's work that *the rate of inversion of cane sugar is not rigidly proportional to the concentration of the hydrogen ions if the concentration of the acid is rather large.* This deviation was thought by Arrhenius to be similar to other known cases involving a "neutral salt effect."[3] He expressed the rate of inversion in the form $\rho = am + bm^2$, in which ρ is the reaction velocity, m is the concentration of the hydrogen ions, a is a factor which is constant for all acids, and b varies with the acid. This factor bm^2 gave the so-called "salt effect," it having already been shown by Palmaer[4] that in completely ionized solutions of hydrochloric acid the reaction velocity is practically directly proportional to the concentration of the hydrogen ions for a given concentration of sugar. Now the concentration of the sugar was constant[5] in Ostwald's

[1] Z. physik. Chem., **4**, 246. Lehrbuch der Elektrochemie, **1901**, p. 174. See also Lunden: Z. physik. Chem., **49**, 195.

[2] J. prakt. Chem., [2] **31**, 317.

[3] For the literature on salt catalysis see Arrhenius: Z. physik. Chem., **1**, 110; **4**, 226; **31**, 197. Euler: *Ibid.*, **32**, 348. Ber. d. chem. Ges., **39**, 2726. Koelichen: Z. physik. Chem., **33**, 129. Senter: J. Chem. Soc., **91**, 460, and later papers. Reid: THIS JOURNAL, **21**, 281; **24**, 397; **41**, 483. Spohr: J. prakt. Chem., [2] **32**, 32; **33**, 265. Z. physik. Chem., **2**, 194. Ostwald: J. prakt. Chem., **33**, 219, and papers cited above. Acree and coworkers: THIS JOURNAL, **38**, 259, 489; **39**, 226; **48**, 352; **49**, 116. Ber. d. chem. Ges., **41**, 3208. Stieglitz and coworkers: THIS JOURNAL, **39**, 177, 467, 596, 720. J. Am. Chem. Soc., **32**, 221; **34**, 1687.

[4] Z. physik. Chem., **22**, 492.

[5] Ostwald showed (J. prakt. Chem., [2] **31**, 315) that the velocity of hydrolysis varies considerably with the concentration of the sugar, and Cohen (Z. physik. Chem., **22**, 442) and Arrhenius (*Ibid.*, **28**, 319) pointed out that the reaction velocity is proportional to the gas, or osmotic, pressure of the sugar solution. This variation arises from the fact that the concentration of the water, another reacting constituent generally ignored, varies considerably also. It has been shown more accurately recently by the work of Morse and Frazer (THIS JOURNAL, **34**, 28; **36**, 39; **38**, 175), of Caldwell (Proc. Roy. Soc., London, **74**, 195), *especially* of Rosanoff (J. Am. Chem. Soc., **33**, 1911), of Hudson (*Ibid.*, **30**, 1160; **33**, 885, 889), of Julius Meyer (Z. physik. Chem., **62**, 59; **72**, 117) and others that there is a direct relationship between the osmotic pressure, the mass of sugar per unit mass (kilogram) of water, and the reaction velocity, if all disturbing influences are considered, as Rosanoff has done recently (J. Am. Chem. Soc., **35**, 248).

experiments, and hence there was no change in the effect of the sugar. Inspection shows that the factor bm^2 can therefore be made to represent the *activity of the nonionized acid* (*base or salt*) instead of a "salt effect," and we have already pointed out[1] that all other cases of the so-called "neutral salt effect" may involve the activity of a *nonionized compound.*

If the cane sugar forms with the acid traces of an intermediate salt in the following way:

$$H^+ \times C_{12}H_{22}O_{11} = K \times C_{12}H_{22}O_{11}.H^+$$
$$(C) \text{ complex cation}$$

$$H^+ \times Ac^- \times C_{12}H_{22}O_{11} = K' \times C_{12}H_{22}O_{11} \times HAc =$$
$$K'' \times C_{12}H_{22}O_{11}.HAc$$
$$(N) \text{ complex nonionized salt}$$

the reaction velocity can be expressed approximately by the equations

$$\begin{aligned} dx/dt &= aC + bN \\ &= a' \times H \times sugar + b' \times H \times Ac \times sugar \\ (a) \quad &= (a'm + b'm^2) \times sugar \\ (b) \quad &= [a'm + b''(1-m)] \times sugar \end{aligned}$$

which is exactly the form derived by Arrhenius. *We see then that the Arrhenius "salt factor"[2] for these acids may just as well be due to the activity of the nonionized salt of the sugar or to the activity of the nonionized acid.*

The relation between the equations (*a*) and (*b*) holds if the ionization of the acid follows the mass law. If such is

[1] THIS JOURNAL, **38**, 273; **41**, 475; **48**, 352; **49**, 116.

[2] Stieglitz first used this Arrhenius idea of a "salt effect" to explain the fact that the rate of hydrolysis of imido ester salts is not strictly proportional to the concentration of the imido ester cations. We pointed out five years ago (THIS JOURNAL, **39**, 521) and showed again, by recalculating his data, in October, 1912 (*Ibid.*, **48**, 370), that he had overlooked the possible activity of the nonionized imido ester salts, and he now (J. Am. Chem. Soc., **34**, 1687, 1689, 1690, 1694) finds that he can reinterpret his results fully as well by recognizing the activity of the nonionized imido ester and bromoamide salts. He has shown that our equations accord excellently with his data. By the use of the data given in his earlier papers, we concluded that there is no appreciable "abnormal salt effect" in his reactions. Although his data were fine for the methods generally in use at that time, the ionizations first published by him are several per cent. in error (cf. THIS JOURNAL, **39**, 729, and J. Am. Chem. Soc., **34**, 1691); on this account the earlier reaction velocities are stated by him (J. Am. Chem. Soc., **34**, 1690, footnote) not to agree with the newer ones. There is therefore an "abnormal salt effect" in his reactions, besides the activity of both the ions and the nonionized salts (J. Am. Chem. Soc., **34**, 1690, 1691, 1694).

not the case, the equation (*b*) holds if the *active*[1] complex cation (*C*) and nonionized salt (*N*) are formed from the hydrogen ions, and nonionized acid, and sugar, or if the reaction velocity is a function of the concentration of the sugar and hydrogen ions and nonionized acid.

Arrhenius did not publish the values which he used for *a* and *b*, but he stated that the value used for *a*, the constant for the *hydrogen ions*, was the same for all acids. As far as we can judge, Arrhenius must have used approximately 31.8 for the value for *a* per gram ion per liter. By the use of some such value he showed that there is a *real* value for *b*, and we have interpreted this as evidence that the nonionized acid is active in all of these cases.

Now the ionization values for strong acids, such as hydrochloric, hydrobromic and nitric acids, *do not* apparently obey the mass law and we must therefore use equation (*b*) to determine whether the *nonionized acids* are active. Dr. Marshall used the data published by Ostwald and found the values

[1] Arrhenius (Z. physik. Chem., **4**, 231; **28**, 317. Rothmund: *Ibid.*, **20**, 168) first advanced this excellent idea that a small portion of the molecules of the changing sugar, ester, etc., are *active* and the others *inactive*. He even went so far as to suggest (*Ibid.*, **28**, 322, footnote) that the *active* molecules may be a combination of the sugar with the water, such as $C_{12}H_{22}O_{11}.H_2O$, for example. He saw also (*Ibid.*, p. 323) the *possibility* that not all H ions are *active*, although stating "Nun sind die Wasserstoffionen warscheinlicherweise vollkommen activ . . Folglich wird jede active Rohrzuckermolekel, welche mit einem Wasserstoffion zusammenstösst, zersetzt werden." It is a strange thing that Arrhenius never seemed to *combine* the idea of the *activity of all H ions from acids* with the idea of active cane sugar molecules by assuming a *union* of the *active* H ions with cane sugar or cane sugar and water together, and the formation of an *active complex cation, or system*, $C_{12}H_{22}O_{11}.H^+ + H_2O$ or $H_2O.C_{12}H_{22}O_{11}.H^+$, which yields the end products. Arrhenius assumed the *cane sugar molecules* to be *active*, whereas to-day the leaders in catalysis believe that the combined *sugar-water-hydrogen ion complexes* are the *active* molecules, an idea evolved from the discovery of the basic properties of oxygen by Collie and Tickle (J. Chem. Soc., **75**, 710) and Baeyer and Villiger (Ber. d. chem. Ges., **34**, 2692; **35**, 1201). Both ideas lead to practically the same results, kinetically, in those cases involving only a trace of active salt, but the later hypothesis is the only one tenable when considerable amounts of the *intermediate active compound* are present. Bredig first suggested *in a footnote*, as a result of his study of the catalytic decomposition of hydrogen peroxide by iodides, (Z. Elektrochem., **9**, 118), that in the catalysis of esters and cane sugar by acids the hydrogen ions combine with the ester or cane sugar and form an intermediate complex *oxonium cation* which is then hydrolyzed. See Stieglitz (Congress Arts and Sciences, St. Louis, 1904, and later papers), where, as a result of his very fine work on imido ester salts, the relation of intermediate *oxonium cation* formation to catalysis received its first full quantitative interpretation in a way to agree with the main facts of the catalysis of esters. See also later work by Bredig on this subject (Z. Electrochem., **10**, 582; **11**, 528. Z. physik. Chem., **47**, 185; **60**, 202). They both overlooked, however, the activity of the *nonionized salts*, which was brought out first by Acree and Johnson (THIS JOURNAL, **37**, 410; **38**, 258).

$K_i = 31.2$ and $K_m = 83.8$ for hydrochloric acid, $K_i = 31.4$ and $K_m = 93.4$ for hydrobromic acid, and $K_i = 31.4$ and $K_m = 73.1$ for nitric acid. *These give us nearly the same values for K_i for the hydrogen ion from all three acids*, as we should get, and show furthermore that K_m, *the activity of the nonionized acid, or nonionized sugar salt, is from 2 to 3 times that of the hydrogen ions.* By the use of the best values we get $K_i = 30.9$, 30.6 and 30.8, respectively, for the hydrogen ion, which are as close to the above as the errors permit. By the use of the values of K_i and K_m given above, Dr. Marshall recalculated the values for K_n and we give the results in the following tables:

Hydrochloric Acid and Sugar

$K_i = 31.2$ $K_n = 83.8$

Conc. of acid	α	K_m found	K_n calc.
0.5 N	0.809	41.0	41.2
0.1 N	0.953	33.4	33.7
0.01 N	1.000	31.3	31.2

Hydrobromic Acid and Sugar

$K_i = 31.4$ $K_m = 93.4$

Conc. of acid	α	K_n found	K_n calc.
0.5 N	0.805	44.7	43.5
0.1 N	0.951	34.1	34.4
0.01 N	1.000	31.8	31.4

Nitric Acid and Sugar

$K_i = 31.4$ $K_m = 73.1$

Conc. of acid	α	K_n found	K_n calc.
0.5 N	0.811	40.2	39.3
0.1 N	0.953	33.1	33.4
0.01 N	1.000	31.7	31.4

The agreement between the calculated and found values is just as good as Arrhenius published and shows that we can fully as well interpret the results as proving that *the nonionized acid, or nonionized sugar salt, enters into the reaction to a much greater extent than does the hydrogen ion.* Both the reaction velocities and ionizations published by Ostwald, although fine for their day, could be improved and we should expect to

secure better concordance with better experimental data. There is no necessity for discussing these details further here.

We have furthermore made some calculations by applying Equation (*b*) to the results obtained by Ostwald with the organic acids (formic, acetic, propionic, butyric and succinic) and have found a *very small activity* for the nonionized organic acids. We consider these results of Ostwald for the organic acids to be less reliable than those obtained by the use of the stronger acids, and hence do not reproduce our data here (see p. 355).

In the same article referred to above Arrhenius[1] studied the effect of salts as well as nonelectrolytes (*Nichtleitern*!) on the inversion of cane sugar by hydrochloric and nitric acids by using various salts and methyl alcohol, ethyl alcohol, acetone, mercuric chloride, and *the nonionized forms of the organic acids*. When he added varying concentrations of the alcohols, acetone and organic acids to 0.005 N and 0.05 N hydrochloric acid and to 0.05 N nitric acid, he found that the alcohols had practically no effect but that *the nonionized forms of formic, succinic, acetic, propionic and butyric acids in every case increase the reaction velocity above the calculated amount.* Now we have interpreted this so-called "effect of these nonelectrolytes" as chiefly the catalytic activity of the nonionized organic acids or of the nonionized salt of the sugar discussed above (see page 351, Equations (*a*) and (*b*)), the alcohol naturally having no such activity. The total change observed may be due partially to a real "abnormal salt effect," resulting from changes in the physical properties of the solutions and to other causes. Arrhenius calculated that one gram molecule each of nonionized formic, succinic, acetic, propionic and butyric acids increases the activity of 0.05 N nitric acid by the amounts represented by 13.2, 9.9, 11.7, 9.2 and 6.7, the activity of the 0.05 N nitric acid being represented by 29.8 at 39°.3.

If we assume, from Arrhenius' data, that the activity of a gram of hydrogen ions per liter is at least 20 × 29.8, or roughly 600, we see that the activity of these nonionized organic acids

[1] Z. physik. Chem., 4, 239.

is *far smaller* than that of the hydrogen ion and still smaller than that of the nonionized hydrochloric, hydrobromic and nitric acids, which is exactly the conclusion reached above from the consideration of Ostwald's work (see p. 354). We see, furthermore, that the activity of the series of nonionized monobasic organic acids given in this list is closely parallel to the affinity constants. We call especial attention to this fact[1] that the *nonionized forms* of the *weak* (organic) *acids* have apparently *much smaller* activities than the nonionized forms of the *strong acids*. While we do not place so much reliance on *our purely approximate* recalculation of the data of Ostwald and Arrhenius, we have found in *all* of *our* work, with one or two apparent exceptions, that the activity of *every alkyl halide, or nitrile*, with the nonionized ethylates and phenolates increases uniformly as we go from the weaker to the stronger electrolyte. Since we look upon the ethylates *as bases in alcohol*, and we have found that Koelichen's work seems to show that nonionized barium hydroxide is less active than the nonionized form of a stronger base, sodium hydroxide, it may be found later to be a general rule that in a given series of reactions the activity of the nonionized form is a function of the affinity constant of the given acid, base or salt. This fact will be found of great importance, probably, in the study of energy changes, whereby even the exceptions may be brought into harmony with the more general rule.

Ostwald,[2] Arrhenius,[3] Spohr,[4] Warder,[5] and Reicher[6] studied the rate of saponification of various esters of acetic acid by weak and strong bases, and both Ostwald and Arrhenius showed that there was excellent agreement between the concentration of the hydroxyl ions, whatever the nature of the base, and the rate of saponification of the ester. This work and that of Osaka,[7] of Bredig and Will,[8] as well as that of

[1] Bredig: Z. Elektrochem., **18**, 543.
[2] J. prakt. Chem., [2] **35**, 112.
[3] Z. physik. Chem., **1**, 110; **2**, 290.
[4] *Ibid.*, **2**, 194.
[5] THIS JOURNAL, **3**, 203, 294, 340. Ber. d. chem. Ges., **14**, 1361.
[6] Ann. Chem. (Liebig), **228**, 257.
[7] Z. physik. Chem., **35**, 661.
[8] Ber. d. chem. Ges., **21**, 2777; see also Gazz. chim. ital., **30**, II, 476.

Koelichen,[1] discussed below, had such a profound influence on chemists that nearly every one to-day believes that all bases react through their hydroxyl ions alone. This belief has probably been greatly strengthened by the electrochemical work involving the relation between the electromotive force and the concentration of the hydroxyl ions.[2] Even though it may be true that the saponification of many esters takes place through the activity of the hydroxyl ions, and does not appreciably involve the nonionized bases, it does not follow that *all* reactions of bases involve *only* the hydroxyl ions. This is well illustrated by the following example which shows that the purely ionic conception of reactions perhaps misled Ostwald in the interpretation of some of the studies carried out in his laboratory.

At Ostwald's suggestion, Koelichen made a beautiful study of the reversible condensation of acetone by alkalis into diacetone alcohol, and they interpreted their results on Ostwald's idea that only the hydroxyl ions are catalytically active. A close inspection of their work shows that their reaction velocities were uniformly larger than those calculated from Ostwald's idea that only the hydroxyl ions are active, and really prove that *both sodium hydroxide and barium hydroxide react through both their hydroxyl ions and the nonionized bases.* In the following tables we give a recalculation of their data by the use of our equations and the values $K_i = 0.2315$ and $K_m = 0.2315$ for sodium hydroxide and $K_i = 0.232$ and $K_m = 0.150$ for barium hydroxide. These approximations seem to show that the hydroxyl ion shows the same activity per gram ion in both cases, but that nonionized barium hydroxide is *less active* in this case than is nonionized sodium hydroxide. The use of our theory and equations gives values (K_v' calc.) involving uniformly smaller experimental errors than those (K_v calc.) calculated by the use of Ostwald's theory, as the following tables show:

[1] Z. physik. Chem., **33**, 129.

[2] Lorenz and Böhi: Z. physik. Chem., **66**, 733. Lewis: *Ibid.*, **55**, 449. Brönsted: *Ibid.*, **65**, 84. For a fine collection of the literature see Abegg, Auerbach, und Luther: "Messungen elektromotorischer Kräfte galvanischer Ketten, **1911**."

Sodium Hydroxide and Diacetone Alcohol

$K_i = 0.2315$ $K_m = 0.2315$

Conc. of NaOH	0.0942	0.0471	0.01884	0.00942	0.00471	(0.002355)
α	0.92	0.956	0.977	0.986	0.995	(1.000)
K_v found	0.02181	0.01110	0.004372	0.002222	0.001053	(0.000445)
K_v calc.	(0.02181)	0.001121	0.004585	0.002313	0.001166	(0.000586)
Error in per cent.	0.00	—0.99	—4.64	—4.10	—10.73	(—31.70)
K_v' calc.	0.02181	0.01090	0.004361	0.002181	0.001090	(0.000545)
Error in per cent.	0.00	+1.8	+0.25	+1.8	—3.5	(—19.0)

Barium Hydroxide and Diacetone Alcohol

$K_i = 0.232$ $K_m = 0.150$

Conc. of $Ba(OH)_2$	0.0942	0.0471	0.01884	0.00942	0.00471
α	0.85	0.89	0.94	0.975	0.99
K_v found	0.02036	0.01083	0.004226	0.002168	0.001061
Error in per cent.	+2.1	+3.8	—4.15	—5.2	—8.6
K_v' calc.	0.02072	0.01050	0.004277	0.002167	0.001088
Error in per cent.	—1.71	+3.1	—1.2	+0.06	—2.5

These tables, and our reinterpretation of the work of Stieglitz and Schlesinger on the decomposition of imido esters by barium hydroxide, discussed in the next article on page 372, show very clearly that the *possibility* of the reaction of the *nonionized bases* should be considered in all such cases.[1]

Then, too, the work of Blanksma[2] on the rearrangement of acetylchloroaminobenzene in the presence of hydrochloric acid showed that the reaction velocity *is not* proportional to the concentration of the hydrogen ions, or complex cations, as was assumed by Arrhenius and Ostwald to be the case in practically all of the studies published then on "the hydrolysis of such weak bases as esters, amides, amidines, oximes" and in "the formation and saponification of esters, and the hydrolysis of acetamide,"

$$CH_3CONClC_6H_5 + \overset{+}{H} \rightleftarrows \underset{\text{cation not appreciably active}}{CH_3CONHClC_6H_5} \longrightarrow CH_3CONHC_6H_4Cl + \overset{+}{H}$$

$$CH_3COOCH_3 + \overset{+}{H} + H_2O \rightleftarrows \underset{\text{cation chief substance transformed}}{CH_3COOCH_3.\overset{+}{H}} + H_2O \longrightarrow CH_3COOH + \overset{+}{H} + CH_3OH$$

but that the reaction velocity *is* nearly proportional to the *square* of the concentration of the hydrogen ions, or product of the concentrations of the hydrogen and chloride ions, and hence, *on our interpretation*, to the concentration of the *nonionized salt* formed by the union of the acetylchloroaminobenzene with *both ions*, or the nonionized acid, as follows:

$$CH_3CONClC_6H_5 + \overset{+}{H} + \overset{-}{Cl} \rightleftarrows \underset{\text{nonionized salt}}{CH_3CONHCl_2C_6H_5} \longrightarrow CH_3CONHC_6H_4Cl + \overset{+}{H} + \overset{-}{Cl}$$

This interpretation was fully justified by later work in 1906–7 by Johnson[4] and Acree on the action of hydrochloric and hydro-

[1] Regarding the possible activity of the ions and molecules of sulphydrates, which are analogous to hydroxides, see the next article, THIS JOURNAL, **49**, 371.

[2] *Loc. cit.*

[3] Johnson and Acree: THIS JOURNAL, **37**, 411, 412.

[4] *Ibid.*, **37**, 410; **48**, 358.

bromic acids on acetylchloroaminobenzene and acetylbromoaminobenzene.

The work of van Dam[1] showed us clearly that in the rearrangement of benzbromoamide by alkalies *both* the *ions* and the *nonionized salt* are transformed into the end products, as discussed in a former communication.[2] Van Dam had interpreted his studies[3] as a pure catalysis by the hydroxyl ions alone.

$$C_6H_5CONBrH + KOH \longrightarrow \begin{cases} \left.\begin{matrix} C_6H_5\overline{C}ONBr \\ \text{and} \\ C_6H_5C(\overline{O}):NBr \end{matrix}\right\} \rightarrow C_6H_5N:C:O + \overline{Br} \\ \left.\begin{matrix} C_6H_5CONKBr \\ \text{and} \\ C_6H_5C(OK):NBr \end{matrix}\right\} \rightarrow C_6H_5N:C:O + KBr \end{cases}$$

Goldschmidt[4] found that the rate of change of diazoaminobenzene in aniline is directly proportional to the concentration of the added aniline hydrochloride. We interpreted this reaction in 1907[5] and again recently[6] as, at least partially, a reaction of the nonionized hydrochloride of the diazoaminobenzene analogous to the rearrangement of acetylchloroaminobenzene by hydrochloric acid,

$$(C_6H_5NH_2.HCl + C_6H_5N:NNHC_6H_5 \rightleftarrows C_6H_5N:NNH_2ClC_6H_5 + C_6H_5NH_2) \longrightarrow C_6H_5N:NC_6H_4NH_2.HCl$$

In 1905 Bredig and Stern[7] published a quantitative study of the condensation of benzaldehyde into benzoin by cyanides, which they interpreted as a *pure* catalysis of the cyanide ions

[1] Rec. trav. chim., **18**, 408; **19**, 318.

[2] Acree: THIS JOURNAL, **45**, 358.

[3] Stieglitz later (Ber. d. chem. Ges., **43**, 783) began an investigation along this same line to see "ob nicht etwa *nur das Ion* umlagerungsfähig ist" (italics ours!) but has recently (J. Am. Chem. Soc., **34**, 1688) come to the conclusion that *both the ions* and the *nonionized salt* rearrange, as we had pointed out at the Boston meeting of the A. A. A. S. in 1909 and again recently (THIS JOURNAL, **45**, 358).

[4] Ber. d. chem. Ges., **21**, 1016, 2557; **28**, 1347; **29**, 1369, 1899. Z. physik. Chem., **29**, 89; **70**, 627. Ann. Chem. (Liebig), **351**, 108.

[5] THIS JOURNAL, **39**, 523, lines 20–21. Goldschmidt has since then (Z. physik. Chem., **70**, 643) interpreted the reaction as one involving the *nonionized* aniline hydrochloride.

[6] THIS JOURNAL, **45**, 368.

[7] Z. Elektrochem., **10**, 582.

alone.[1] *They assumed a constant per cent. of ionization* for 66 per cent. alcoholic solutions of potassium cyanide varying from 0.4 N to 0.05 N. This assumption is, of course, extremely improbable, as the ionization increases very greatly in such a case.

Since their reaction velocities, per gram molecule of potassium cyanide, did not increase noticeably with increasing ionization, we[2] have been able to show that their results really harmonize with our theory that *the cyanide ions and the nonionized potassium cyanide are, in this case, equally active, and that* K_i *and* K_m *are about 0.089.*

$$2C_6H_5CHO + \overline{CN} \longrightarrow C_6H_5COCH(OH)C_6H_5 + \overline{CN}$$
$$2C_6H_5CHO + KCN \longrightarrow C_6H_5COCH(OH)C_6H_5 + KCN$$

In 1905 Tubandt[3] published a fine study of the catalytic reversible inversion of *d*- and *l*-menthones by sodium ethylate, which he did not interpret in terms of the ionization theory. We have shown[4] that his work harmonizes excellently with our theory and that *both the ethylate ions and the nonionized sodium ethylate* invert the menthone with the same velocity; namely, 0.41 at 20° and 0.93 at 30° for each gram ion or molecule per liter.

These were the chief organic[5] reactions with which we were familiar in 1905 and which *seemed* to involve both the ions and the nonionized forms of acids, bases or salts. These reactions showed, to say the least, a *deviation* from a purely ionic reaction, which Arrhenius and others interpreted as a "salt effect," but which we interpreted as *partially*, at least, an

[1] Bredig and Walton (Z. Elektrochem., **9**, 114. Z. physik. Chem., **47**, 185) showed in a very pretty study that sodium, potassium and ammonium iodides cause the pure *catalysis* of hydrogen peroxide with a velocity which is nearly proportional to the concentration of the *iodide ions*. Since cadmium iodide decomposes hydrogen peroxide more rapidly than they calculated from their theory, the writer suggests that the *cadmium iodide molecules* may be active. Unfortunately not enough is now known concerning the ionization of such ternary electrolytes.

[2] THIS JOURNAL, **48**, 380.

[3] Ann. Chem. (Liebig), **339**, 41; **354**, 259; **377**, 284.

[4] THIS JOURNAL, **48**, 379.

[5] We have noted a number of *inorganic* reactions, oxidations, reductions, etc., which seem to involve both ions and nonionized electrolytes, and we shall discuss these later in a special article.

actual activity of the nonionized substances. In April,[1] 1907, and September,[2] 1907, we published a preliminary report introducing the theory that *both*[3] *ions and nonionized salts, acids and bases must be considered in all reactions*, and have since then been steadily at work on this theory. We realized at that time the seriousness of our assumption, an assumption made in the face of such eminent men, and for that reason we did not care to reinterpret their work then. We preferred to work out a number of different reactions very accurately and establish the idea firmly on an experimental basis. Perhaps because of its very novelty the idea has been considered and passed over by many others. Even after we published our first report with some experimental evidence others perhaps questioned the theory and failed to use it, but have gradually come to the same idea, as the following examples illustrate.

Lapworth wrote me recently as follows: "At the time I read your first catalysis paper, and controversy with Stieglitz, this considerable advance on the theoretical side made by you must have made no lasting impression on me, in spite of the fact that Stieglitz acknowledged the fact it was novel. Perhaps *because* of its novelty I dismissed it too hastily in reading."

Stieglitz has pointed out in letters and in his publications[4] that he overlooked at first the importance of the suggestion. This is shown by the fact that after we *emphasized*[5] *71 times*, in equations and formulas and words, in one article alone, the activity of the nonionized electrolytes in 1907, he published a number of very fine papers[6] in 1908 interpreting his work on imido ester salts as reactions of ions alone and has only recently,[7] after we pointed out the possibility of the activity of his non-

[1] THIS JOURNAL, **37**, 410.

[2] *Ibid.*, **38**, 258.

[3] We included "acids, bases and salts" in 1907 in the above articles and THIS JOURNAL, **39**, 155, 226, and many other places in which we pointed out that *pure* catalysis and *pseudo* catalysis are fundamentally alike, but we have confined our attention chiefly to the reactions of the bases and salts.

[4] *Ibid.*, **39**, 402, 403.

[5] In *Ibid.*, **38**, 258, and many other articles.

[6] THIS JOURNAL, **39**, 177, 467, 596, 720. J. Am. Chem. Soc., **32**, 221.

[7] *Ibid.*, **34**, 1687, 1688, 1689, 1690, 1694.

ionized[1] salts, come to realize that he can give a better reinterpretation of his imido ester reactions and the Beckmann rearrangement by recognizing the activity of the nonionized salts.

In 1908 Goldschmidt[2] wrote a discussion of our work on the action of the alkyl halides on the urazole salts,[3] but considered only the ions. Although our articles to which he referred (1907–8) contained full discussions of the activity of the *nonionized salts*, Goldschmidt apparently neglected this fact and it was not till 1909–10 that he at last fully realized the importance of the idea and began[4] to use it to reinterpret his own work.

In his very complete and thoughtful review of catalysis in 1909, Bodenstein[5] discussed our idea that ions may react but failed entirely to mention the nonionized salts. This is all the more noticeable when we consider the fact that he discussed, on page 412, the rearrangement of acetylchloroaminobenzene, the very reaction which we emphasized in this connection.

In 1908 Bredig wrote me several letters dealing with catalysis, discussing in particular our theory that the nonionized salt of acetylchloroaminobenzene rearranges. He raised the objection that in such cases the really *active* system may be *base* + *H* + *Cl* instead of the nonionized salt, *base.HCl*, and did not believe that we can tell whether the nonionized salt, or both the ions together, undergoes transformation. He has now, however, come to the other point of view and is now[6] using the same theory and equations[7] to reinterpret his reactions of acids and diazoacetic ester. He formerly[8] thought that only the hydrogen ions act catalytically, but he now

[1] THIS JOURNAL, **39**, 521; **48**, 371.

[2] Z. Elektrochem., **15**, 10.

[3] Ber. d. chem. Ges., **41**, 3206, 3210, 3211, 3213, 3214. THIS JOURNAL, **37**, 410; **38**, 258, 489.

[4] Z. Elektrochem., **15**, 6. Z. physik. Chem., **70**, 627.

[5] Z. Elektrochem., **15**, 390.

[6] Bredig: *Ibid.*, **15**, 535, 543.

[7] Cf. Brunel and Acree: THIS JOURNAL, **42**, 519 (1910), and Bredig and Snethloge: Z. Elektrochem., **18**, 540 (1912).

[8] Bredig and Praenkel: *Ibid.*, **11**, 525 (1905); Z. physik. Chem., **60**, 202 (1907).

believes that *both* the *hydrogen ions* and the *nonionized acid* are active.

A number of articles have been published recently by Senter,[1] Holmberg,[2] Rivett,[3] and others which seem to involve nonionized salts. Deserving of especial attention is an article by L. W. Jones on the Beckmann rearrangement,[4] the treatment of which shows the thoughtful care and fine spirit back of all his work. In the last year H. C. Biddle[5] has shown that nonionized acids are active in a number of important reactions involving alkaloids and dyes. In the field of enzyme work, Hudson[6] has shown in a number of important papers the effect of hydrogen ions and hydroxyl ions on the activity of invertase and emulsin.

When we proposed the theory of the activity of both ions and nonionized electrolytes we saw that much more work was needed involving *very accurate measurements* of (1) the *reaction velocities*, of (2) the *true ionization* of the reacting electrolytes and of (3) the so-called "salt effect"[7] which had been noticed in a number of cases by Arrhenius, Euler, Spohr and others. Since a large change in the per cent. of ionization is absolutely necessary in order to allow us to measure *most accurately* the activity of the ions and of the nonionized substances, we chose ethyl and methyl alcohols as the chief solvents for our work. There is a far greater change in ionization in ethyl alcohol, as we go from N/1 to N/1000 solutions, than is the case in aqueous solutions. The work in our laboratory has now shown that in a number of cases we seem beyond doubt to be dealing with the reactions of both ions and nonionized electrolytes in both concentrated and dilute solutions, so we shall begin now to publish in about twenty articles the preliminary portion of the work and shall make the final corrections of our constants

[1] J. Chem. Soc., **91**, 460; **95**, 1827; **97**, 346; **99**, 95; **101**, 2528, 2534. Ber. d. chem. Ges., **45**, 2318.

[2] Z. physik. Chem., **79**, 147, 621. Ber. d. chem. Ges., **45**, 3000.

[3] Z. physik. Chem., **83**, 201.

[4] THIS JOURNAL, **48**, 1.

[5] Ber. d. Chem. Ges., **45**, 526, 2832. J. Am. Chem. Soc., **34**, 500; **35**, 273.

[6] J. Am. Chem. Soc., **30**, 1160, 1564; **31**, 655, 1136, 1242; **32**, 774, 1220, and later papers.

[7] For references see p. 350.

later when we study the effects of fluidity, solvation, complex salt formation, and other uncertain physical factors.

In order to bring up to date the evidence which we have obtained I give a few tables of some of the constants obtained by my various coworkers. If both the ethylate ions and the nonionized portions of sodium, potassium and lithium ethylates react with alkyl halides as follows:

$$\overline{O}C_2H_5 + C_2H_5I \rightleftarrows \underset{I}{C_2H_5\overline{O}C_2H_5} \longrightarrow (C_2H_5)_2O + \overline{I}$$

$$NaOC_2H_5 + C_2H_5I \rightleftarrows \underset{I}{C_2H_5\,\overset{Na}{O}\,C_2H_5} \longrightarrow (C_2H_5)_2O + NaI$$

and the results are analyzed by means of the equation[1]

$$dx/dt = [K_i\alpha + K_m(1-\alpha)]\,(C_{salt} - x) \times (C_{alkyl\ halide} - x)\,(1 + (f)\,C_{salt}),$$

we should find the same values for K_i, the activity of a gram equivalent of ethylate ions with a certain alkyl halide, whether we use sodium, potassium or lithium ethylate. Of course, the values of K_m, the activity of a gram equivalent of the nonionized ethylate salt, would vary, because the nonionized molecules of sodium, potassium and lithium ethylates are different. The theory[2] has been fully substantiated by the work of Dr. Julia P. Harrison, Dr. E. K. Marshall, Jr., and Mr. J. H. Shrader on the action of ethyl bromide on sodium, potassium and lithium ethylates in solutions varying from N/1 to N/32. The conductivities and ionization of all the following salts at 0°, 25°, and 35° were measured by Dr. H. C. Robertson, Jr.:

	K_i	K_m
Dr. Marshall: Sodium ethylate and ethyl bromide	0.00576	0.00233
Dr. Harrison: The same	0.00557	0.00232
Dr. Harrison: Potassium ethylate and ethyl bromide	0.0055	0.0029
Mr. Shrader: Lithium ethylate and ethyl bromide	0.0057	0.00157

[1] For the development and use of these equations, see especially THIS JOURNAL, **37**, 410; **38**, 258; **43**, 519; **48**, 353.

[2] For a preliminary report of part of the following work, see THIS JOURNAL, **48**, 352.

Although the reaction velocities and ionizations of these three salts vary widely, these values of K_i are identical within the experimental errors, as they should be. But the values of K_m for the nonionized sodium, potassium and lithium ethylates vary widely, in accordance with our theory. *The activity of the nonionized salts* is from 30 per cent. to 55 per cent. of that of the ethylate ion.

Similar evidence has been obtained by Dr. Marshall, Dr. Harrison and Mr. Shrader in the study of the action of ethyl iodide on sodium, potassium and lithium ethylates.

	K_i	K_m
Dr. Marshall: Sodium ethylate and ethyl iodide	0.0120	0.00427
Mr. Shrader: The same	0.0122	0.0040
Dr. Harrison: Potassium ethylate and ethyl iodide	0.0121	0.0047
Mr. Shrader: Lithium ethylate and ethyl iodide	0.01215	0.0030

The reaction velocities and ionization of these salts vary widely, but the values for K_i for the ethylate ion and ethyl iodide are practically the same for all three ethylates, as they should be. The values for K_m for the *nonionized ethylates vary* from 25 per cent. to 38 per cent. of the value of K_i, in accordance with the theory.

The same kind of proof has been obtained by Dr. H. C. Robertson, Jr., Dr. Harrison and Miss B. Marion Brown in their studies of the reactions of methyl iodide with sodium and potassium ethylates.

	K_i	K_m
Dr. Robertson: Sodium ethylate and methyl iodide	0.127	0.0589
Miss Brown: The same	0.127	0.0594
Dr. Harrison: Potassium ethylate and methyl iodide	0.1264	0.0676

The theory is substantiated fully as well here as in the other studies, and Miss Brown is continuing these investigations at 0° and 35°.

	K_i	K_m
Miss Brown: Sodium ethylate and methyl iodide at 0°	0.0049	0.0030
Miss Brown: Lithium ethylate and methyl iodide at 0°	0.0052	0.0020
Miss Brown: Potassium ethylate and methyl iodide at 0°	0.0053	0.0034

Dr. Robertson and Mr. J. H. Shrader have obtained excellent evidence that methyl iodide, ethyl iodide and allyl bromide react at 25° and 35° with *both the ions and nonionized portions of sodium, potassium and lithium phenolates*.

	K_i	K_m
Dr. Robertson: Sodium phenolate and methyl iodide at 25°	0.0282	0.0047
Mr. Shrader: Potassium phenolate and methyl iodide at 25°	0.0283	0.0037
Mr. Shrader: Lithium phenolate and methyl iodide at 25°	0.0284	0.0040
Dr. Robertson: Sodium phenolate and methyl iodide at 35°	0.091	0.0131
Dr. Robertson: Sodium phenolate and ethyl iodide at 25°	0.0056	0.00099
Mr. Shrader: Potassium phenolate and ethyl iodide at 25°	0.0052	0.00101
Mr. Shrader: Lithium phenolate and ethyl iodide at 25°	0.00534	0.00091
Dr. Robertson: Sodium phenolate and ethyl iodide at 35°	0.0184	0.00323
Mr. Shrader: Potassium phenolate and ethyl iodide at 35°	0.0197	0.0027
Mr. Shrader: Lithium phenolate and ethyl iodide at 35°	0.0174	0.0032

The values of K_i for the reaction of methyl iodide with sodium, potassium and lithium phenolates at 25°, and of K_i for ethyl iodide with sodium, potassium and lithium phenolates at 25° and 35°, are identical within the experimental errors. The values of K_m for the nonionized salts vary, in accordance with the theory. It will be observed that the ratios $K_i : K_m$ for the phenolates vary from 5 to 7 and are much larger than the ratios $K_i : K_m$ for the ethylates.

In other articles[1] it was pointed out that Dr. F. M. Rogers and Dr. Sidney Nirdlinger found in 1908 that *ethyl iodide reacts at 25° with both the anion and the nonionized form of sodium 1-phenyl-3-thiourazole.* They obtained the values $K_i = 0.435$ and $K_m = 0.17$. Dr. Joseph Chandler has repeated their work under somewhat better conditions and obtained the values $K_i = 0.465$ and $K_m = 0.16$, which are in substantial agreement with the above.

Dr. E. K. Marshall and Dr. Julia P. Harrison have shown that sodium, potassium and lithium ethylates cause the reversible change of acetimido ethyl ester and benzimido ethyl ester into the corresponding nitriles and ethyl alcohol. *The ethylate ions and nonionized sodium ethylate are both catalytically active.* For acetimido ethyl ester and sodium ethylate Dr. Marshall finds the values $K_i = 0.344$ and $K_m = 0.228$, while for benzimido ethyl ester Dr. Harrison finds the values $K_i = 0.1172$ and $K_m = 0.0976$. The experimental work forms the basis of the following article.

In all of the above studies the concentrations were varied from N/1 to N/32 or N/64, but these solutions cannot be considered *ideal.* Dr. C. N. Myers has therefore undertaken the study of the reversible addition of ethyl alcohol to *p*-bromobenzonitrile, and the catalytic effect of sodium, potassium and lithium ethylates in solutions as dilute as N/2048. He finds that our theory holds excellently in these *ideal solutions* (N/32 to N/2048) and he obtains the rounded values $K_i = 0.160$ and $K_m = 0.160$ for sodium ethylate, $K_i = 0.160$ and $K_m = 0.141$ for potassium ethylate, and $K_i = 0.161$ and $K_m = 0.087$ for lithium ethylate. In the N/32 solutions the sodium ethylate reacts 50 per cent. faster than does the lithium ethylate, because the sodium ethylate is more highly ionized and the ethylate ions and nonionized sodium ethylate molecules react faster than do the nonionized lithium ethylate molecules. But all three salts are practically completely ionized in the N/2048 solutions, in which the concentrations of the ethylate ions are therefore practically alike. Hence these three salts should show, and actually do have, the same activity in these dilute

[1] This Journal, **43**, 519, 551; **49**, 116.

(N/2048) solutions. The work on the tetramethyl ammonium ethylate, $(CH_3)_4\overset{+}{N}\overset{-}{O}C_2H_5$ is in progress, and agrees in the main with these ideas, and the preliminary work on thallium ethylate shows it to be much less active than even the lithium ethylate, in accordance with the theory.

It is thus seen that our theory of the activity of *both ions and nonionized electrolytes seems to hold in both concentrated and ideal solutions*. We realize (1) that our values for K_i and K_m for the concentrated solutions contain a small "abnormal salt effect" in some cases, (2) that the abnormal fluidity of the solutions, complex ions and salts, and the solvation of the electrolytes make the value $\mu_v : \mu_\infty$ an inaccurate measure of the per cent. of ionization, and (3) that the abnormal physical properties of these solutions may influence all of the data. These effects, however, are much the same for solutions of similar concentrations with all of these ethylates, phenolates, etc., and the values for K_i and K_m for corresponding sodium, potassium and lithium salts will doubtless be changed very much alike. We are studying all of these reactions in the *ideal solutions*, and are measuring the physical factors, just as rapidly as possible, and shall make the final corrections later in our completed articles.

It is therefore clear that all of our work and our reinterpretation of the work of Arrhenius, Ostwald, Bredig, Goldschmidt, Stieglitz, Blanksma, van Dam, and others, gives evidence that *both ions and nonionized electrolytes, and nonionizable substances, may be concerned in all chemical reactions*. In so far as the activity of the *ions* is proven in our work we have brought new evidence to place Arrhenius' brilliant theory of ionization, and Ostwald's conception of the activity of ions, on a more secure basis. In so far as the activity of the *nonionized electrolytes* is established we have added evidence to the newer theory. But all of this is merely a beginning. In order to learn how and why chemical reactions take place we must look far deeper than the mass law and the theory of electrons, down into the changes of energy within the atoms and molecules.

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ON THE REACTIONS OF BOTH THE IONS AND THE NONIONIZED FORMS OF ELECTROLYTES THE REVERSIBLE ADDITION OF ALCOHOLS TO NITRILES CATALYZED BY SODIUM ETHYLATE, II

By E. K. Marshall, Jr., Julia Peachy Harrison and S. F. Acree

[SIXTEENTH COMMUNICATION ON CATALYSIS]

(We are indebted to the Carnegie Institution of Washington for aid in these researches.)

Sodium ethylate has long been used as a catalyzer[1] in the inversion of menthone, in the acetoacetic ester synthesis and allied reactions, in the study of the reactions of alcohols with nitriles[2] by Nef, Stieglitz and Dains, and especially Stieglitz and McKee, and McKee, and of alcohols with mustard oils, acid chlorides, alkyl halides and in many other cases. The *quantitative* study of the mechanism of these reactions is of the greatest importance not only to the organic chemist but to all other chemists. In connection with other investigations along these lines we have taken up the *quantitative*[3] study of the addition of alcohols to nitriles in order (1) to learn whether the reactions are reversible and to measure the equilibrium points, and (2) to study the exact nature of the mechanism of the action of sodium ethylate, and other ethylates, especially in the light of our other work with ethylates, phenolates, etc., which has shown that

[1] Vorländer: Ber. d. chem. Ges., **36**, 268. Karl Elbs: Kohlenstoff-Verbindungen, **1889**, p. 34. Marshall and Acree: This Journal, **49**, 130. Hofmann: Ber. d. chem. Ges., **2**, 120; **3**, 772. Bamberger: *Ibid.*, **15**, 2164. Schiff: *Ibid.*, **9**, 1316. Wurtz: Ann. chim. phys., [3] **42**, 43. Kremann: Monats. Chem., **26**, 783; **29**, 23. Claisen: Ber. d. chem. Ges., **20**, 646. Kossel, Krüger and Obermüller: Z. physiol. Chem., **15**, 321; **16**, 153. Purdie: J. Chem. Soc., **39**, 344; **47**, 863, 867; **59**, 469. Friedländer and Mähly: Ann. Chem. (Liebig), **229**, 210.

[2] Nef: Ann. Chem. (Liebig), **287**, 280. Dains: J. Am. Chem. Soc., **31**, 136. McKee: This Journal, **28**, 209; **36**, 209; **42**, 1.

[3] Dr. Marshall's work was completed in 1911 and Dr. Harrison's in 1912. We had hoped to complete this investigation by studying the action of potassium and lithium ethylates on benzimido ethyl ester and acetimido ethyl ester to learn whether the same value for K_1 is obtained for all ethylates, and different values for K_m are found. Since both Dr. Harrison and Dr. Marshall have been compelled to withdraw from the work it seems best for their interests to publish this incomplete study at this time. The final corrections will be made when these studies are completed.

we can express the reaction velocities as functions of the concentrations of both the ethylate ions and the nonionized sodium ethylate.

In another article[1] we have shown that in every case studied the reaction

$$RC : N + C_2H_5OH \rightleftarrows RC(:NH)OC_2H_5$$

does not take place appreciably of itself, but, when catalyzed by ethylates, is reversible. The equilibrium point is the same whether measured from the nitrile or from the imido ester, although slow disturbing side reactions make the agreement in some cases less satisfactory than desired. The equilibrium point varies very widely with the different compounds. The per cent. of imido ester formed is illustrated by the following examples: butyronitrile, 0.90; propionitrile, 1.75; acetonitrile, 2.50; *p*-tolunitrile, 6.8; benzonitrile, 14.0; *p*-chlorobenzonitrile, 25.85; *p*-bromobenzonitrile, 27.2; *m*-bromobenzonitrile, 38.5; *p*-nitrobenzonitrile, 62.0; *m*-nitrobenzonitrile, 78.0; diisoamylcyanoamide, 98.0. The equilibrium point varies rather widely in some cases with changes in the concentrations of the nitrile and the ethylate, but fluctuates very little in other examples. Different ethylates catalyze the reaction with different velocities and the equilibrium points also often vary in such cases. The velocity of the reaction varies greatly with the different nitriles, the *p*-nitrobenzonitrile and chloroacetonitrile reacting very rapidly, whereas *o*-tolunitrile hardly adds alcohol at all.

With this point settled, *we turned our attention to the question whether the sodium ethylate reacts catalytically through the influence of the ethylate ions, or the nonionized sodium ethylate, or both.* This problem and analogous ones are of all the more interest to us because the sodium ethylate acts catalytically in the older sense in that it brings about its chemical changes by its mere presence and is not appreciably changed in its activity, whereas in the reactions with alkyl halides the sodium ethylate is entirely transformed into the end products. It was all the more desirable to us to study

[1] Marshall and Acree: THIS JOURNAL, **49**, 127.

this and other similar reactions, therefore, to connect these limiting cases in which, on the one hand, the catalyzer is apparently not changed at all, with those in which, on the other hand, it is completely decomposed. It is of the highest importance that we have connected these limiting cases experimentally and shown that fundamentally there is no primary difference in the mechanism of the action of sodium ethylate in the two cases, the *apparent* dissimilarities really depending on a secondary factor, the stability or neutrality of intermediate products, and the tendency of the particular solution to yield the most nearly neutral system. This can be illustrated readily in such equations as the following:

$$\left\{\begin{array}{l} C_2H_5\bar{O} + IC_2H_5 \rightleftarrows C_2H_5O.IC_2H_5 \longrightarrow \bar{I} + (C_2H_5)_2O \\ C_2H_5\bar{O} + CH_3C : N \rightleftarrows CH_3C(:\bar{N})OC_2H_5 + C_2H_5OH \longrightarrow \\ \qquad\qquad CH_3C(:NH)\bar{O}C_2H_5 + C_2H_5\bar{O} \end{array}\right.$$

$$\left\{\begin{array}{l} C_2H_5ONa + IC_2H_5 \rightleftarrows C_2H_5ONa.IC_2H_5 \longrightarrow NaI + (C_2H_5)_2O \\ C_2H_5ONa + CH_3C : N \rightleftarrows CH_3C(:NNa)OC_2H_5 + \\ \qquad\qquad C_2H_5OH \longrightarrow CH_3C(:NH)OC_2H_5 + NaOC_2H_5 \end{array}\right.$$

Stieglitz and Schlesinger[1] have studied, in aqueous solutions, the reverse of this reaction, the decomposition of imido esters, in the presence of barium hydroxide as catalytic agent. They followed the ideas of Arrhenius,[2] Ostwald,[3] van't Hoff,[4] Warder,[5] Reicher,[6] Spohr,[7] Hemptinne,[8] Löwenherz,[9] and others, who had shown that ordinary esters are saponified by bases (and acids) with a velocity approximately proportional to the concentration of the hydroxyl[10] (and hydrogen) ions. As

[1] THIS JOURNAL, **39**, 719 (1908).
[2] Z. physik. Chem., **1**, 110 (1887).
[3] J. prakt. Chem., [2] **28**, 449 (1883).
[4] Etudes de dynamique chimique.
[5] THIS JOURNAL, **3**, 340 (1882).
[6] Ann. Chem. (Liebig), **228**, 257 (1885).
[7] Z. physik. Chem., **2**, 194 (1888).
[8] *Ibid.*, **13**, 561 (1894); **21**, 35 (1899).
[9] *Ibid.*, **15**, 395 (1894).
[10] Miss Marion Brown is now engaged on the analogous study of the saponification of thioesters by sodium, potassium, lithium, ammonium, etc., sulphydrates in absolute ethyl alcohol in order to learn whether both the ionized and nonionized sulphydrates react with the thioesters. The much smaller ionization of these salts in alcohol will allow us to measure the possible activity of the nonionized sulphydrates much better than can be done in aqueous solutions in which the concentration of the nonionized sulphydrate is much smaller than in alcoholic solutions of the same concentration.

a result of their very fine experimental work, they came to the conclusion that an imido ester is decomposed completely into a nitrile and an alcohol *with a velocity proportional to the concentration of the hydroxyl ions and anions of the imido ester.* Stieglitz has admittedly[1] overlooked a principle brought out by one of us, namely, that the *nonionized compounds*, such as barium hydroxide and barium imido ester salts, may be concerned in such reactions. It can be shown that Stieglitz's excellent work harmonizes better with our theory than with his, and that our work, in which we can more accurately measure all the necessary data, leads to the belief that he has perhaps interpreted his experiments unfortunately in that he did not consider the fact that BOTH *the nonionized barium hydroxide and the hydroxyl ions, and nonionized and ionized imido ester salts, may be concerned in the reaction.*

Before our own work was undertaken we examined Stieglitz's data and saw that we secure constants just as good as his if we assume that $K_i = K_m$ for barium hydroxide and that a *gram molecule of nonionized barium hydroxide is just as effective in decomposing imido esters as is a gram ion of hydroxyl ions.* The reasons for the apparent equal validity of these two different interpretations of the experimental work of Stieglitz and Schlesinger is that in the solutions studied the barium hydroxide is so nearly completely ionized, 93 to 97.5 per cent., that the small influence of the nonionized portion, 2.5 to 7 per cent., is masked by the experimental errors necessarily involved in even this fine work. These uncertainties are apparent when we see that the widest variation in K_V in a given series sometimes becomes as high as 23 and 25 per cent., as in Tables XXV*b* and XV*b*, and averages about 9 per cent. for all of the series.

In the following tables we have given the essential details of Tables XX, XXIV, XXVIII, XXXII and XXXVI in Schlesinger's article. In the first column are given the concentrations of barium hydroxide used, in the second the value of K_V, in the third the value K_{OH}, or K_i, obtained by

[1] THIS JOURNAL, **39**, 403. J. Am. Chem. Soc., **34**, 1688, 1689, 1690, 1694.

Schlesinger, in the fourth the deviation of each number in Column 3 from the mean of the entire column, in the fifth the constants calculated simply from the concentration of the barium hydroxide on our assumption that perhaps $K_i = K_m$, and in the sixth the deviation of each number in Column 5 from the mean of the entire column. We did not take the trouble to refer the constants in Column 5 to the same units used by Schlesinger but give simply the quotients of corresponding numbers in Columns 1 and 2. The errors involved in the two methods of calculation, as shown in Columns 4 and 6, are the points of real interest.

Table XX

Conc. of $Ba(OH)_2$	K_V	K_i Schlesinger	Error in per cent. Schlesinger	K_m	Error in per cent.
5.90	102	0.887	+3.86	17.28	+5.56
5.80	100	0.885	+3.75	17.24	+5.31
11.40	193	0.873	+2.23	16.93	+4.03
12.00	203	0.871	+1.99	16.91	+3.91
31.80	511	0.837	—1.99	16.07	—1.83
31.10	497	0.833	—2.46	15.98	—2.38
46.60	742	0.840	—1.64	15.92	—2.75
(48.00)	(741)	(0.812)	(—4.92)	(15.44)	(—5.69)
70.20	1090	0.835	—2.23	15.53	—5.13
70.60	1090	0.830	—2.81	15.44	—5.69
		0.854		16.37	

Table XXIV

Conc. of $Ba(OH)_2$	K_V	K_i Schlesinger	Error in per cent. Schlesinger	K_m	Error in per cent.
35.90	205	0.298	—0.67	5.71	—0.175
35.70	202	0.298	—0.67	5.66	—1.049
52.20	299	0.301	+0.33	5.73	+0.175
53.50	310	0.290	—3.33	5.79	+1.223
70.10	401	0.307	+2.33	5.72	±0.000
70.40	402	0.307	+2.33	5.71	—0.175
		0.300		5.72	

Table XXVIII

Conc. of $Ba(OH)_2$	K_V	K_i Schlesinger	Error in per cent. Schlesinger	K_n	Error in per cent.
30.50	152	0.255	+6.69	4.98	+9.45
30.70	171	(0.285)	....	....	....
61.50	255	0.220	—7.90	4.54	—0.22
64.30	291	0.241	+0.83	4.55	0.00
45.60	207	0.339	0.00	4.15	—8.79
46.20	210	0.239	0.00	4.53	—0.43
		0.239		4.55	

Table XXXII

Conc. of $Ba(OH)_2$	K_V	K_i Schlesinger	Error in per cent. Schlesinger	K_n	Error in per cent.
30.90	67.6	0.114	0.00	2.19	+0.92
32.20	67.5	0.109	—4.38	2.10	—3.22
46.20	101	0.115	+0.88	2.19	+1.38
46.50	109	0.123	+7.90	2.34	+7.83
61.50	130	0.113	—0.88	2.11	—2.76
61.60	128	0.111	—2.63	2.08	—4.15
		0.114		2.17	

Table XXXVI.

Conc. of $Ba(OH)_2$	K_V	K_i Schlesinger	Error in per cent. Schlesinger	K_n	Error in per cent.
32.70	510	1.62	+0.62	15.6	+1.30
43.70	690	1.66	+3.11	15.8	+2.60
62.50	930	1.55	—3.72	14.9	—3.25
		1.61		15.4	

When these tables are inspected it is seen that the errors in Columns 4 and 6 are uniformly of the same magnitude. Table XX is the least satisfactory one given by Schlesinger, the variations in a given series amounting to 25 per cent. in some cases. If Table XX is omitted, the average of all the values given in Column 4 is 2.14 per cent., while that of Column 6 is identically the same. If Table XX is included, the average of Column 4 is 2.25 per cent. and that of Column 6 is 2.71 per cent. When we recall that the average maximum variation of the constants in a series is 9 per cent., it is seen that

this difference between 2.71 per cent. and 2.25 per cent. is well within the experimental errors. We could be as fully justified, therefore, in believing that barium hydroxide acts through *both* its nonionized form and the hydroxyl ions, as are Stieglitz and Schlesinger in using the theory that the imido esters are decomposed by hydroxyl ions alone in a way shown by Arrhenius, Ostwald, and others to hold for ordinary esters, and our work on the ethylates presented in the following paragraphs leaves no doubt that our point of view is preferable.

For this reason we have chosen alcohol for use as the solvent, whenever possible, for studying reactions; the nonionized salt is present in much larger concentrations and its influence can be measured with much greater accuracy. Our own work in alcoholic solutions has shown that the velocity of decomposition of imido esters is a function of the concentrations of *both* the ethylate ions and the sodium ethylate molecules, the values $K_i : K_m = 0.1172 : 0.0976$ and $K_i : K_m = 0.344 : 0.228$ having been found for benzimido ethyl ester and acetimido ethyl ester, for example. We consider that, in this case, as in others, sodium, potassium and other ethylates are *bases* in ethyl alcohol analogous to the corresponding hydroxides in water. If we were to work with sodium ethylate solutions more dilute than 0.002 N, the per cent. of ionization of the ethylate would be found to be above 90 per cent., and, as in Stieglitz's work with barium hydroxide, the reaction velocities would be so nearly proportional to the concentration of the ethylate ions that the activity of the sodium ethylate molecules would be masked by experimental errors to just the same extent observed in the work of Stieglitz and Schlesinger with barium hydroxide. Fortunately we can work with solutions as concentrated as 0.25 N, in which the relative concentration of the ethylate ions is only about 30 per cent. and that of the nonionized sodium ethylate 70 per cent., and in which the change due to the molecules is about 20 times as large as in 0.002 N solutions and hence easily measured. Our work shows the interpretation of Stieglitz to be *partially* correct in that it proves that imido esters are decomposed by

hydroxyl (and ethylate) ions, and further substantiates the still broader theory that both ions and nonionized compounds must be considered in the study of all reaction mechanisms.

If the rate of reaction of the imido ester, or of the nitrile, is practically zero in the *absence* of ethylates, and in their *presence* it is a function of the concentrations of both the ethylate ions and the nonionized sodium ethylate, the reaction velocity must be expressed by the equation,

$$\frac{dx}{dt} = K_i\,[K'_i\alpha + K'_m(1-\alpha)] \times C_{ethylate} \times (A_1 - x)$$
$$- K_2\,[K'_i\alpha + K'_m(1-\alpha)] \times C_{ethylate} \times (A_2 + x)$$

in which it is assumed that the concentration of the alcohol is practically a constant, involved in K_2, that α is the per cent. of ionization of the sodium ethylate, $C_{ethylate}$, that K'_i is the catalytic effect of the ethylate ions, that K'_m is the catalytic effect of the nonionized sodium ethylate, that A_1 is the original concentration of the imido ester, that A_2 is the original concentration of the nitrile, and that x is the change in concentration of the imido ester in the time t. The integral of this equation is

$$K_V = \frac{1}{t}\ln\frac{KA_1 - A_2}{KA_1 - A_2 - (K+1)x} =$$
$$\frac{(K_1 + K_2)[K'_i\alpha + K'_m(1-\alpha)] \times C_{ethylate}}{[K_i\alpha + K_m(1-\alpha)] \times C_{ethylate}}$$

in which

$$K = \frac{K_1[K'_i\alpha + K'_m(1-\alpha)] \times C_{ethylate}}{K_2[K'_i\alpha + K'_m(1-\alpha)] \times C_{ethylate}} = \frac{K_1}{K_2}, \text{ and}$$
$$K_i = K'_i(K_1 + K_2), \text{ and } K_m = K'_m(K_1 + K_2).$$

It is to be noted that in developing these equations we have assumed the ratios $K_i : K_m$, for the reverse reactions, to be constant, an assumption which leads to the conclusion that K must be constant. We actually find K to be constant within the experimental errors, and hence independent of the concentration of the sodium ethylate. We have developed similar equations to apply to those cases in which K varies. K_V should be constant with varying concentrations of nitrile and a constant concentration of sodium ethylate, provided

that no double compounds are formed, and the nitrile does not visibly alter the physical properties of the solutions. As a matter of experiment we find in Table XIX an increase of only 7.4 per cent. in K_V with an increase of 800 per cent. in the concentration of acetonitrile. We have therefore used only one concentration of nitrile, 0.250 N, in all of the quantitative studies. In the remainder of the article we shall use the expressions K_i and K_m instead of K'_i $(K_1 + K_2)$ and K'_m $(K_1 + K_2)$ merely for convenience. Having then obtained the different values K_V, K'_V, K''_V, for the different concentrations of sodium ethylate, $1/V$, $1/V'$, $1/V''$, etc., we need only multiply the different values of K_V by the values for the corresponding V and we obtain a series of simultaneous equations:

$$K_n = K_i\alpha + K_m(1 - \alpha),$$
$$K'_n = K_i\alpha' + K_m(1 - \alpha'),$$
$$K''_n = K_i\alpha'' + K_m(1 - \alpha''), \text{ etc.,}$$

in which K_n, K'_n, K''_n, etc., given in Table XIX, represent the reaction velocities which would be found if the solution were *normal* with respect to sodium ethylate having the degree of ionization α, α', α'', etc. When these equations are solved we obtain in Table XX the values 0.344 and 0.228 for K_i and K_m for acetimido ethyl ester, which are constant within the experimental errors, the ratio $K_i : K_m$ being approximately 1.5. In Table X in the work on benzimido ethyl ester we find the values 0.1172 and 0.0976 for K_i and K_m. This is entirely in harmony with our work on the action of alkyl halides on sodium ethylate, on sodium phenolate and sodium 1-phenyl-3-thiourazole, in which we have found that we can express the reaction velocities as functions of the concentrations of the ions and of the nonionized salts. The ratios $K_i : K_m$ are 2.13, 2.81 and 2.41 for the reaction of sodium ethylate with methyl iodide, ethyl iodide and ethyl bromide, respectively. We have furthermore substituted the values 0.344 and 0.228 in the various equations, $K_n = K_i\alpha + K_m$ $(1-\alpha)$, $K'_n = K_i\alpha' + K_m$ $(1-\alpha')$, etc., corresponding to the different values of α, α', α'', etc., and have obtained values for "K_n calculated" which are shown in Table XXI to agree very closely

with the "K_m found" obtained experimentally. We may conclude then that, in some respects, sodium ethylate behaves toward the unsaturated nitriles, $CH_3C:N$, just as it does towards the unsaturated alkyl halides, $CH_3I\equiv$, an unstable addition product probably being formed as an intermediary step in both cases on account of the unsaturated character of all these substances.

But we have fortunately been able to go one step further in this work. When we examine the above equations we see that we could look upon the reactions as an *acceleration* of the purely *ionic* reaction by another reaction which we have called the nonionic reaction, whose coefficient is K_m. This *salt effect* is a very important phase of reaction mechanisms, is not very well understood at present, and has been a subject of investigation by us in all of our quantitative studies with the urazoles, amides, ethylates, etc., etc., and it has furthermore received attention from a large number of other workers. Arrhenius[1] suggested that this salt effect is due to the ions of the salt, and Euler[2] believed that these ions change the ionization of water and hence influence the rate of those reactions in which water is one of the reacting constituents. Stieglitz has adopted these ideas and applied them to his fine imido ester work.[3] He thinks that he has found evidence for the support of their theories, especially the idea of Euler, and believes that the "salt effect" of the cation is chiefly only a change in the active mass, or per cent. of ionization, of the water. But we have shown in another article[4] that Stieglitz has perhaps made an unfortunate interpretation of his own experimental work. His experimental data have been recalculated by us and found to give a full and complete verification of our ideas of "salt catalysis" rather than of those of Arrhenius and Euler, and prove that the "salt effect" is chiefly the transformation of the nonionized imido ester salt, augmented by an "abnormal salt catalysis."

[1] Z. physik. Chem., **1**, 110 (1887).

[2] *Ibid.*, **33**, 357 (1900).

[3] THIS JOURNAL, **30**, 437 (1908); **39**, 586; **39**, 719. J. Am. Chem. Soc., **32**, 222 (1910).

[4] THIS JOURNAL, **48**, 369; **49**, 120.

$$C_6H_5C(:\overset{+}{N}H_2)OC_2H_5 + H_2O \longrightarrow$$

$$C_6H_5C(OH)(\overset{+}{N}H_3)OC_2H_5 \longrightarrow C_6H_5COOC_2H_5 + \overset{+}{N}H_4$$

$$C_6H_5C(:NH_2Cl)OC_2H_5 + H_2O \longrightarrow$$

$$C_6H_5C(OH)(NH_3Cl)OC_2H_5 \longrightarrow C_6H_5COOC_2H_5 + NH_4Cl$$

Starting from the idea that the "salt effect" may be due to another reaction involving nonionized complex compounds, perhaps in traces in some cases, we have developed the above equation, $K_n = K_i\alpha + K_m(1 - \alpha)$, to express such a reaction when the nonionized salt (*e. g.*, sodium ethylate) forms the nonionized complex, and also the alternate equation, $K_n = K_i\alpha + K_m(\alpha^2/V)$ which applies if the *nonionized* complex compound is formed from the *anion and cation* together. We have shown in another paper[1] that the first equation applies in all cases whereas the second applies in only two cases, which may be due to *algebraical accidents*. It will now be shown that the first equation applies very closely in the present work, whereas the second equation leads to no constants at all.

Let us take the case of a solution of 0.25 N acetimido ethyl ester and 0.0625 N sodium ethylate for which we used the equation $K_n = K_i\alpha + K_m(1 - \alpha)$, and the found values $K_n = 0.2848$, $\alpha = 0.481$, $K_i = 0.344$ and $K_m = 0.228$. If the equation $K_n = K_i\alpha + K_m(\alpha^2/V)$ were true, then the addition of sodium iodide to this solution of sodium ethylate and imido ester should suppress the ionization of the sodium ethylate in accordance with the isohydric principle, which we have proven experimentally, and should therefore decrease the value of $K_i\alpha$. But the *decrease* in α, the concentration of the ethylate ion, is small in comparison with the *increase* in α/V, the concentration of the sodium cations. If, for instance, we were to add 7 equivalents of sodium iodide to 0.0625 N sodium ethylate and 0.25 N acetimido ethyl ester, the ionization of the sodium ethylate should change from that of a N/16 solution, 0.481, to that of a N/2 solution, 0.234, in accordance with the isohydric principle, and the value of $K_i\alpha$ would change from $0.344 \times 0.481 = 0.1655$ to $0.344 \times 0.234 = 0.0805$, a decrease of 51 per cent. But if we use

[1] THIS JOURNAL, **48**, 376.

the calculated value, about 8, for K_m, the value of $K_m(\alpha^2/V)$ would change from 0.118 to $8 \times 0.234 \times 0.169 = 0.3164$, an increase of about 168 per cent. As a consequence, then, the value of K_n should *increase* from 0.2848 found to 0.3969, or 39 per cent., when 7 equivalents of sodium iodide are added. If the total change were one of the cations and anions together in one reaction, increased by the cations in another reaction, the rate, K_v, would change from 0.0178, found, for the 0.0625 N sodium ethylate alone, to about 0.0778, an increase of 337 per cent. by the 7 equivalents of sodium iodide. If the reaction were one of sodium ethylate molecules, increased by another reaction of the cations, the velocity would change from 0.0178 found for the 0.0625 N sodium ethylate alone, to 0.0690 in the presence of 7 equivalents of sodium iodide, *an increase of 288 per cent.* As a matter of fact it *decreases* to 0.2512, and no one of these three hypotheses holds in our work. We have also tried, without success, to apply the formulas $K_n = K_i\alpha + K_m$, $K_n = K_i + K_m(1-\alpha)$, to a number of cases. When we finally collect our experimental material we shall again consider all of these hypotheses.

But let us calculate what should be the change if our alternate theory holds, and the equation $K_n = K_i\alpha + K_m(1-\alpha)$ represents the true course of all the reactions studied, even when an *added* salt changes the reaction velocity through the so-called "salt catalysis." As stated above, the value of $K_i\alpha$ should be changed from $0.344 \times 0.481 = 0.1655$ to $0.344 \times 0.234 = 0.0805$, and the value $K_m(1-\alpha)$ should consequently be changed from $0.288 \times 0.519 = 0.118$ to $0.228 \times 0.766 = 0.1745$. K_n consequently should be changed from $0.344 \times 0.481 + 0.228 \times 0.519 = 0.2838$ to $0.344 \times 0.234 + 0.228 \times 0.766 = 0.2551$. We find actually experimentally 0.2512 which differs from this calculated value only 1.6 per cent. but differs by 58 per cent. from the 0.3969 calculated on the first of the three above assumptions. The same close agreement with our theory is found when varying mixtures of sodium ethylate and sodium iodide, and sodium ethylate and sodium bromide, are used, and we can therefore conclude *that in this case* the mysterious so-called

"salt catalysis" is nothing more than a change, produced by the added salt, in the concentrations of the reacting constituents, as demanded by the Arrhenius-Barmwater theory of isohydric solutions.[1]

It is clear then that we have secured some experimental evidence concerning the nature of the catalytic action of added salts in this case and four others and that we can explain the *chief part* of this salt catalysis *in all cases yet studied by us* on the *rational basis* of the transformation of a nonionized complex compound formed by the reaction of, for example, the imido ester and the nonionized catalyzer, or on the basis of the reaction of the *nonionized catalyzer* with the imido ester *directly*, without the assumption of the formation of a complex compound. In the case of sodium ethylate, sodium phenolate, sodium thiourazole, and imido ester salts, the nonionized salt is present in large amounts and disappears in the reaction with the alkyl halide or water, the addition products,

$$C_2H_5I.C_2H_5ONa,\ C_2H_5C(OH)(NH_2Cl)(OC_2H_5),\ \text{etc.},$$

perhaps, forming the intermediate steps. In the case of the *pure* catalysis of the imido ester, or nitrile and alcohol, by sodium ethylate the nonionized salt does not disappear in the reaction, and yet the "salt effect" is due *solely* to the increase in the concentration of the *nonionized* sodium ethylate, which is also approximately true in the above cases in which the nonionized compound disappears as a result of the reaction: there is, however, a small "abnormal salt effect" in these latter cases. In some other reactions as pointed out before, it may be found that the "salt catalysis" is produced on account of the formation of complex compounds, in *traces* in some cases, from certain constituents and *anions and cations together*, while in still other cases the salt catalysis may be due to the formation of other anions or cations, or nonionized complex salts, having reaction velocities greater or smaller than those of the original constituents. The formulas

$$C_6H_5C(:NH_2Cl)(OC_2H_5).KCl,\quad C_6H_5C(:NH_2Cl)(OC_2H_5).\overset{+}{H},$$

$$C_2H_5ONa.C_2H_5I.NaI \text{ and } C_2H_5ONa.IC_2H_5.\overset{+}{Na}$$

[1] Z. physik. Chem., **28**, 424 (1899). *Ibid.*, **45**, 557 (1903).

are illustrations of the idea. The variations of this central idea are manifold. The question then whether the *added salt* will *increase* or *decrease* the reaction velocity will naturally depend simply upon the relative magnitudes of K_i and K_m, or other constants involved. If, for instance, K_m is the larger, the addition of the *added or catalyzing salt increases* the reaction velocity because the increase in the concentration of the nonionized form of the reactive salt causes the increase in $K_m(1 - \alpha)$ to be larger than the attendant decrease in $K_i\alpha$. The added salt suppresses the ionization of the active salt, and *lowers* the reaction velocity when K_i is larger than K_m because the decrease in $K_i\alpha$ is then greater than the increase in $K_m(1 - \alpha)$. This last case corresponds to all the problems that we have yet studied and to our interpretation of Stieglitz's imido ester work. If $K_m = K_i$ the added salt cannot change the reaction velocity, unless for reasons other than the ones discussed here. There may be "abnormal salt effects" in many cases, some of which we are studying.

This idea of salt catalysis is far more fortunate than the *assumption* by Euler and Stieglitz that the added salt changes the active mass, or per cent. of ionization, of the water or alcohol to a considerable extent. All the evidence is against any such idea that the water can change more than a very few per cent. in ionization, and their theory is clearly wrong for the reasons pointed out in earlier articles.[1]

EXPERIMENTAL

Acetonitrile and Acetimido Ethyl Ester

The bath used in this investigation has already been described.[2] Its temperature was constant at 25° to within ±0°.005. The alcohol used was dehydrated by boiling it with lime. No alcohol was used which contained more then 0.06 per cent. water, and in general the amount of water was considerably less than this. The *acetimido ethyl ester hydrochloride* was prepared as already described in another article.[3] The solutions of sodium ethylate were prepared by dissolving

[1] See especially THIS JOURNAL, **41**, 475; **48**, 369.
[2] H. C. Robertson, Jr.: Diss., Johns Hopkins Univ., **1910**.
[3] Marshall and Acree: THIS JOURNAL, **49**, 146.

pure sodium in cold alcohol. The measurements of the velocity of the reaction were carried out as follows: A solution of the required strength of acetimido ethyl ester hydrochloride was made by weighing the substance, transferring it to a graduated flask, dissolving it in alcohol as quickly as possible, and diluting the solution to the mark at 25°. A solution of sodium ethylate was prepared having the required strength plus the amount necessary to liberate the free imido ester from its hydrochloride. Thus, if 0.25 N imido ester and 0.25 N sodium ethylate were required, equal volumes of a 0.5 N solution of imido ester hydrochloride and N solution of sodium ethylate were mixed. The time of mixing the two solutions was noted, and aliquot portions (10 or 20 cc.) were pipetted out at various intervals and titrated with standard hydrochloric acid. The equilibrium point was determined by two duplicate titrations after the solution had stood overnight or longer. The equilibrium point from the imido ester side did not correspond to that obtained by starting with the nitrile. This is due to three causes: (1) to a small amount of ammonium chloride present in the original imido ester hydrochloride, (2) to the decomposition of the solution of the imido ester hydrochloride into ortho-ester and ammonium chloride during the short time necessary for bringing it to 25° and diluting the solution, and (3) to the decomposition of the imido ester hydrochloride into acetamide and ethyl chloride during this short time. The ammonia thus formed when the sodium ethylate solution is added remains practically constant throughout the reaction. The concentration of the ethylate is not influenced by this, and as the values for x with varying t are obtained from the difference in the alkalinity of the solution, x is therefore not affected. The only error to be taken into consideration is the value of A, or the concentration of the imido ester. This can be corrected for by considering the equilibrium point obtained by starting with the nitrile as the true one. For instance, we see in Table I that with 0.25 N acetonitrile and 0.5 N, 0.25 N, 0.125 N, and 0.0625 N sodium ethylate an average of 1.73 per cent. imido ester is formed at equilibrium. If our value of A_1 is 12.50, we have

$12.50 \times 0.0173 = 0.21$ as the amount of imido ester which should be present in the solution at equilibrium. This would give us as the equilibrium value of x $12.50 - 0.21 = 12.29$, but the value found for x is 12.13. We have, therefore, a correction for the ammonia formed amounting to 0.16. This gives us as a correct value for A, $12.50 - 0.16 = 12.34$. The amount of ammonia varies somewhat, as would be expected, in the individual experiments, but on an average amounts to a little over one per cent. The correction for the change in concentration of the imido ester has been applied in all cases.

We first proved that the free imido ester does not decompose with any appreciable velocity unless catalyzed by the ethylate. A solution of the imido ester hydrochloride was treated with nine-tenths of the theoretical amount of ethylate and titrated from time to time by Dr. C. N. Myers.

Time	3.5 hrs.	4 hrs.	23 hrs.	29 hrs.	46 hrs.	9 days
Cc. 0.2 N HCl	9.77	9.70	9.71	9.70	9.71	9.31

The amount of change due to the *uncatalyzed*, or spontaneous decomposition of the free imido ester cannot produce any appreciable error in our constants. When portions of this solution were treated with N/8 sodium ethylate the imido ester was decomposed as usual.

Since the mass of the alcohol can be considered practically constant, we have a reversible monomolecular reaction expressed by the following equations:

$$\frac{dx}{dt} = K_1(A_1 - x) - K_2(A_2 + x)$$

in which A_1 is the original concentration of the imido ester, A_2 that of the nitrile, and x the concentration of the nitrile formed during the reaction. At equilibrium, we have

$$K = \frac{K_1}{K_2} = \frac{A_2 + x}{A_1 - x}$$

Substituting K for K_1/K_2 we get

$$\frac{1}{t} \ln \frac{KA_1 - A_2}{KA_1 - A_2 - (K+1)x} K_1 + K_2 = K_V.$$

Since $A_2 = 0$ in all our experiments, we can simplify the above expression and obtain

$$\frac{1}{t} \ln \frac{KA_1}{KA_1 - (K+1)x} = K_1 + K_2 = K_V$$

in which

$$K = \frac{x}{A_1 - x}$$

K_n is obtained by dividing K_V by the concentration, $1/V$, of the sodium ethylate. All concentrations in this work are those obtained *after mixing* the solutions. The two following tables on acetonitrile and sodium ethylate are taken from a previous article[1] by the authors.

Table I—0.25 N Acetonitrile[2] and Sodium Ethylate

Conc. sodium ethylate	Per cent. imido-ester formed
0.5 N	1.68
0.25 N	1.80
0.125 N	1.64
0.0625 N	1.80
0.03125 N	1.60
0.015625 N	1.60
Average used =	1.73

Table II—Acetonitrile and Sodium Ethylate

Conc. aceto-nitrile	Conc. sodium ethylate	Per cent. imido-ester formed
0.5 N	0.5 N	1.44
0.25 N	0.25 N	1.80
0.125 N	0.25 N	2.48
0.0625 N	0.25 N	2.56

Table III—Ionization of Sodium Ethylate in Absolute Alcohol at 25°

V	α	$(1-\alpha)$
1	0.148	0.852
2	0.234	0.766
4	0.312	0.688
8	0.393	0.607
16	0.481	0.519
32	0.577	0.423
64	0.686	0.314

[1] Marshall and Acree: THIS JOURNAL, **49**, 149.

[2] The last two values were worked out by Dr. C. N. Myers.

Table IV[1]*—0.25 N Acetimido Ethyl Ester and 0.25 N Sodium Ethylate*

$A_1 = 12.34$	$A_2 = 0$	$K = 55.1\ (57.8)$[2]
t	x	K_V
25	10.11	0.0689
31	10.71	0.0693
37	11.18	0.0689
46	11.61	0.0684
	12.13	
		Average = 0.0689
		$K_n = 0.2756$

Table V—0.25 N Acetimido Ethyl Ester and 0.25 N Sodium Ethylate

$A_1 = 12.05$	$A_2 = 0$	$K = 54.0\ (56.4)$
t	x	K_V
21	9.06	0.0691
28	10.15	0.0695
34	10.66	0.0680
40	11.04	0.0675
	11.84	
		Average = 0.0685
		$K_n = 0.2740$

Table VI—0.25 N Acetimido Ethyl Ester and 0.125 N Sodium Ethylate

$A_1 = 12.22$	$A_2 = 0$	$K = 60.0\ (57.2)$
t	x	K_V
5	1.98	0.0359
15	4.79	0.0339
27	7.10	0.0332
40	9.41	0.0382
91	11.41	0.0332
	12.01	
		Average = 0.0341
		$K_n = 0.2728$

[1] The values in Tables IV and V are not used in the final calculations because in these concentrations the abnormal physical properties become noticeable. Dr. Meyers has obtained similar results in his work on the addition of ethyl alcohol to *p*-bromobenzonitrile in the presence of sodium, potassium and lithium ethylates.

[2] The values of K given outside the parentheses in each of the following tables are those calculated from the data for the corresponding concentrations in Table I, the values inside the parentheses being derived from the *average used*, 1.73. The influence of K in the formula is so small that identically the same reaction velocity is obtained by the use of either value of K.

Table VII—0.25 N Acetimido Ethyl Ester and 0.125 N Sodium Ethylate

$A_1 = 12.30$	$A_2 = 0$	$K = 60.4\ (57.6)$
t	x	K_V
5	2.07	0.0375
15	5.03	0.0359
25	6.91	0.0339
40	8.96	0.0339
60	10.52	0.0341
90	11.53	0.0341
	12.09	

Average = 0.0349
$K_n = 0.2792$

Table VIII—0.25 N Acetimido Ethyl Ester and 0.125 N Sodium Ethylate

$A_1 = 12.23$	$A_2 = 0$	$K = 60.1\ (57.2)$
t	x	K_V
10	3.52	0.0345
17	5.20	0.0334
23	6.44	0.0334
31	7.70	0.0330
45	9.35	0.0334
60	10.46	0.0341
90	11.42	0.0336
	12.02	

Average = 0.0336
$K_n = 0.2688$

Table IX—0.25 N Acetimido Ethyl Ester and 0.0625 N Sodium Ethylate

$A_1 = 12.23$	$A_2 = 0$	$K = 54.7\ (57.2)$
t	x	K_V
15	2.90	0.0184
25	4.33	0.0179
35	5.51	0.0175
50	7.01	0.0175
66	8.23	0.0174
126	10.73	0.0177
147	11.10	0.0174
	12.02	

Average = 0.0177
$K_n = 0.2832$

Table X—0.25 N Acetimido Ethyl Ester and 0.0625 N Sodium Ethylate

$A_1 = 12.27$	$A_2 = 0$	$K = 54.8\ (57.4)$
t	x	K_V
25	4.39	0.0181
35	5.63	0.0180
45	6.66	0.0179
60	7.93	0.0179
80	9.15	0.0178
115	10.53	0.0179
∞	12.06	
		Average = 0.0179
		$K_m = 0.2864$

Table XI—0.25 N Acetimido Ethyl Ester and 0.03125 N Sodium Ethylate

$A_1 = 12.15$	$A_2 = 0$	$K = 59.7\ (56.9)$
t	x	K_V
15	1.53	0.00914
30	2.91	0.00928
45	4.04	0.00917
65	5.40	0.00924
90	6.74	0.00898
110	7.65	0.00930
156	9.13	0.00928
262	10.92	0.00937
∞	11.94	
		Average = 0.00921
		$K_m = 0.2947$

Table XII—0.25 N Acetimido Ethyl Ester and 0.03125 N Sodium Ethylate

$A_1 = 11.92$	$A_2 = 0$	$K = 58.5\ (55.8)$
t	x	K_V
25	2.44	0.00933
41	3.71	0.00928
56	4.72	0.00921
71	5.63	0.00924
92	6.68	0.00919
122	7.79	0.00898
∞	11.71	
		Average = 0.00919
		$K_m = 0.2941$

Table XIII—0.25 N Acetimido Ethyl Ester and 0.015625 N Sodium Ethylate

$A_1 = 24.44$	$A_2 = 0$	$K = 60.2\ (57.2)$
t	x	K_V
15	1.60	0.00477
30	3.11	0.00477
50	4.91	0.00479
80	7.50	0.00484
104	9.17	0.00479
210	15.03	0.00491
333	18.92	0.00500
∞	24.02	

Average = 0.00484
K_m = 0.3098

Table XIV—0.25 N Acetimido Ethyl Ester and 0.015625 N Sodium Ethylate

$A_1 = 24.36$	$A_2 = 0$	$K = 59.8\ (57.0)$
t	x	K_V
15	1.70	0.00489
30	3.30	0.00491
51	5.21	0.00481
90	8.29	0.00472
207	14.92	0.00474
292	17.82	0.00470
∞	23.94	

Average = 0.00479
K_m = 0.3066

Table XV—0.5 N Acetimido Ethyl Ester and 0.125 N Sodium Ethylate

$A_1 = 24.27$	$A_2 = 0$	$K = 66.4$
t	x	K_V
11	8.35	0.0382
17	11.87	0.0394
26	15.49	0.0389
33	16.70	0.0352
40	18.24	0.0348
60	21.12	0.0341
85	22.80	0.0329
∞	23.91	

Average = 0.0362
K_m = 0.2896

Table XVI—0.5 N Acetimido Ethyl Ester and 0.125 N Sodium Ethylate

$A_1 = 24.07$	$A_2 = 0$	$K = 66.0$
t	x	Kv
25	14.99	0.0401
32	16.59	0.0375
41	18.54	0.0371
53	20.37	0.0368
67	21.70	0.0368
∞	23.70	

Average = 0.0375
K_n = 0.3000

Table XVII—0.125 N Acetimido Ethyl Ester and 0.25 N Sodium Ethylate

$A_1 = 6.07$	$A_2 = 0$	$K = 39.5$
t	x	Kv
8	2.59	0.0719
16	4.00	0.0705
21	4.50	0.0679
27	4.99	0.0684
33	5.31	0.0689
41	5.54	0.0670
54	5.80	0.0721
∞	5.92	

Average = 0.0685
K_n = 0.2740

Table XVIII—0.0625 N Acetimido Ethyl Ester and 0.25 N Sodium Ethylate

$A_1 = 6.09$	$A_2 = 0$	$K = 37.1$
t	x	Kv
15	3.71	0.0661
21	4.43	0.0654
26	4.86	0.0658
32	5.22	0.0663
38	5.44	0.0654
45	5.67	0.0690
50	5.73	0.0672
∞	5.93	

Average = 0.0661
K_n = 0.2644

The concentrations in the above tables are all expressed after mixing. Referring the reaction velocities for the different dilutions to normal concentration, we obtain comparable values, which we shall designate K_n. The following table gives a résumé of all the above work and was used in calculating the values of K_i and K_m given in Table *XX*.

Table XIX—0.25 N Acetimido Ethyl Ester and Sodium Ethylate

Concentration of sodium ethylate	$K_1 + K_2 = K_V$		K_n
0.125 N	0.0341		
	0.0349	0.0342	0.2736
	0.0336		
0.0625 N	0.0177		
	0.0179	0.0178	0.2848
0.03125 N	0.00931		
	0.00919	0.00920	0.2944
0.015625 N	0.00484		
	0.00479	0.00482	0.3084

Acetimido Ethyl Ester and Sodium Ethylate

Concentration of imido ester	Concentration of sodium ethylate	$K_1 + K_2 = K_V$		K_n
0.5 N	0.125 N	0.0362		
		0.0375	0.0369	0.2952
0.5 N	0.25 N	....		0.2852[1]
0.25 N	0.25 N	0.0692		0.2768
0.125 N	0.25 N	0.0685		0.2740
0.0625 N	0.25 N	0.0661		0.2644

If, in this case of catalysis, we have both the ethylate ion and sodium ethylate molecules concerned in the reaction, we should be able to calculate the constant for the velocity of the ionic and molecular reactions separately, as has been done in the case of the reaction between ethylates and alkyl halides.[2] We have used the equation $K_n = K_i\alpha + K_m(1-\alpha)$ in which K_i is the ionic velocity and K_m the molecular velocity, and calculated the following values for K_i and K_m, which are seen to be very constant.

[1] Recalculated from the data for 0.5 N imido ester and 0.125 N sodium ethylate.

[2] See other work by Robertson, Marshall, Harrison, Chandler, Myers, Shrader, Brown, Nirdlinger and Rogers: THIS JOURNAL, **48**, 352; **49**, 116, 127.

Table XX

v	K_i	K_m
8 : 16	0.336	0.238
8 : 32	0.342	0.230
8 : 64	0.346	0.228
16 : 32	0.346	0.228
16 : 64	0.346	0.222
32 : 64	0.348	0.222
	Average, = 0.344	0.228

We have used the values $K_i = 0.344$ and $K_m = 0.228$ in recalculating the values of K_n corresponding to the different concentrations of sodium ethylate used, and have compared these values of "K_n calculated" with those of "K_n found." The agreement is quite satisfactory as can be seen from the following table:

Table XXI—0.25 N Acetimido Ethyl Ester and Sodium Ethylate

Concentration of sodium ethylate	K_n found	K_n calculated	Error in per cent.
0.125	0.2736	0.2736	±0.00
0.0625	0.2848	0.2838	+0.35
0.03125	0.2944	0.2949	—0.10
0.015625	0.3084	0.3076	+0.26
		Average error =	—0.05

A STUDY OF SALT CATALYSIS

After thus learning the effect of the *ethylate ion* and of the *nonionized sodium ethylate* on this reaction, we thought it wise to test this theory further by suppressing the ionization of the sodium ethylate by the addition of sodium iodide in order to see if the new reaction velocities correspond to the new ionization values. This should be the case if the added sodium iodide produces no "abnormal salt effect," the theory of which was discussed fully on page 379. The following tables show, in the main, that the change in the reaction velocity is very close to that calculated from our theory, and that the sodium iodide produces no appreciable "abnormal salt effect." The value of K used was determined experimentally in each case

by measuring the equilibrium point in the corresponding mixture of sodium iodide, sodium ethylate and acetonitrile.

Table XXII—0.25 N Acetimido Ethyl Ester, 0.25 N Sodium Ethylate and 0.25 N Sodium Iodide

$A_1 = 12.45$	$A_2 = 0$	$K = 124$
t	x	K_V
20	9.00	0.0656
26	10.08	0.0651
31	10.70	0.0650
37	11.22	0.0647
44	11.66	0.0654
	12.35	
	Average	= 0.0651
	Calculated	= 0.0638
	K_V without sodium iodide	= 0.0692

0.25 N Acetonitrile and 0.25 N Sodium Ethylate with 0.25 N Sodium Iodide.—Twenty cc. were taken for titration, and required 25.22, 25.24, 25.23 cc. 0.2 N hydrochloric acid. This corresponds to 0.84 per cent. imido ester present at equilibrium.

Table XXIII—0.25 N Acetimido Ethyl Ester and 0.125 N Sodium Ethylate with 0.125 N Sodium Iodide

$A_1 = 12.03$	$A_2 = 0$	$K = 119$
t	x	K_V
32	7.78	0.0329
45	9.13	0.0322
53	9.71	0.0318
61	10.23	0.0320
68	10.61	0.0322
76	10.91	0.0324
	11.93	
	Average	= 0.0322
	Calculated	= 0.0321
	K_V without sodium iodide	= 0.0342

0.25 N Acetonitrile and 0.1245 N Sodium Ethylate with 0.125 N Sodium Iodide.—Twenty cc. were used for titration, and required 12.73, 12.76 cc. 0.2 N hydrochloric acid. This

corresponds to 0.84 per cent. imido ester present at equilibrium.

Table XXIV—0.25 N Acetimido Ethyl Ester and 0.125 N Sodium Ethylate with 0.375 N Sodium Iodide

$A_1 = 12.25$	$A_2 = 0$	$K_V = 122$
t	x	K_V
21	5.97	0.0322
25.5	6.77	0.0320
30	7.41	0.0313
41	8.66	0.0304
48	9.37	0.0306
59	10.12	0.0304
69	10.61	0.0300
∞	12.15	

Average = 0.0310
Calculated = 0.0319
K_V without sodium iodide = 0.0342

0.25 N Acetonitrile and 0.1246 N Sodium Ethylate with 0.375 N Sodium Iodide.—Ten cc. were used for titration and required 6.34, 6.33 cc. 0.2 N hydrochloric acid. This corresponds to 0.84 per cent. imido ester present at equilibrium.

Table XXV—0.25 N Acetimido Ethyl Ester and 0.0625 N Sodium Ethylate with 0.0625 N Sodium Iodide

$A_1 = 12.14$	$A_2 = 0$	$K = 120$
t	x	K_V
16	2.98	0.0178
21	3.68	0.0174
27	4.38	0.0167
36	5.42	0.0166
51	6.86	0.0167
67	8.04	0.0164
108	9.99	0.0164
∞	12.04	

Average = 0.0169
Calculated = 0.0171
K_V without sodium iodide = 0.0178

0.25 N Acetonitrile and 0.616 N Sodium Ethylate with 0.0625 N Sodium Iodide.—Ten cc. were used for titration and re-

quired 3.22, 3.19, 3.20 cc. 0.2 N hydrochloric acid. This corresponds to 0.96 per cent. imido ester present at equilibrium.

Table XXVI—0.25 N Acetimido Ethyl Ester and 0.0625 N Sodium Ethylate with 0.1875 N Sodium Iodide

$A_1 = 12.20$	$A_2 = 0$	$K = 121$
t	x	K_V
16	2.81	0.0165
21	3.46	0.0160
34	4.94	0.0155
43	5.98	0.0162
61	7.43	0.0156
84	8.85	0.0156
126	10.41	0.0156
∞	12.10	

Average = 0.0159
Calculated = 0.0165
K_V without sodium iodide = 0.0178

0.25 N Acetonitrile and 0.0626 N Sodium Ethylate with 0.1875 N Sodium Iodide.—Ten cc. were used for titration and required 3.24, 3.26 cc. 0.2 N hydrochloric acid. This corresponds to 0.96 per cent. imido ester present at equilibrium.

Table XXVII—0.25 N Acetimido Ethyl Ester and 0.0625 N Sodium Ethylate with 0.4375 N Sodium Iodide

$A_1 = 12.10$	$A_2 = 0$	$K = 120$
t	x	K_V
20	3.33	0.0162
27	4.26	0.0162
34	5.03	0.0160
42	5.79	0.0157
50	6.48	0.0155
69	7.79	0.0152
81	8.52	0.0153
∞	12.00	

Average = 0.0157
Calculated = 0.0160
K_V without sodium iodide = 0.0178

0.25 N Acetonitrile and 0.0634 N Sodium Ethylate with 0.4375 N Sodium Iodide.—Twenty cc. were used for titra-

tion and required 6.44, 6.43 cc. 0.2 N hydrochloric acid. This corresponds to 0.74 per cent. imido ester at equilibrium.

In the following table we give a résumé of all the above work on the *salt catalysis* produced by sodium iodide.

Table XXVIII—0.25 N Acetimido Ethyl Ester, Sodium Ethylate and Sodium Iodide

Concentration of sodium ethylate	Concentration of sodium iodide	Kv found	Kv calculated	Error in per cent.
0.250 N	0.250 N	0.0651	0.0638	+2.0
0.125 N	0.125 N	0.0322	0.0321	+0.3
0.125 N	0.375 N	0.0310	0.0319	—3.0
0.0625 N	0.0625 N	0.0169	0.0171	—1.2
0.0625 N	0.1875 N	0.0159	0.0165	—3.8
0.0625 N	0.4375 N	0.0157	0.0160	—1.9

Average error = —1.26

The experiments show very clearly that the "salt effect" produced by the added sodium iodide can be interpreted as due *chiefly* to the change in ionization of the sodium ethylate by the sodium iodide and the resulting change in reaction velocity.

Since the acetimido ethyl ester decomposes so nearly completely into acetonitrile and alcohol in the presence of sodium ethylate, we made some calculations to see whether good constants can be obtained by considering the reaction as monomolecular and considering A to be the total change in the concentration of the imido ester. The following corrected tables show that the constants have practically the same value whether calculated in this way or on the correct basis:

Table XXIX—(See Table VIII)

$A = 12.03$

t	$A - x$	AK
10	8.51	0.0345
17	6.83	0.0333
23	5.59	0.0333
31	4.33	0.0329
45	2.68	0.0332
60	1.57	0.0339

Average = 0.0335

$K_1 + K_2 = 0.0336$

Table XXX—(See Table XVII)

$A = 5.92$

t	$A - x$	AK
8	3.33	0.0633
16	1.92	0.0707
21	1.42	0.0691
27	0.93	0.0690
33	0.61	0.0690
41	0.38	0.0670
54	0.12	0.0721

Average = 0.0686
$K_1 + K_2$ = 0.0685

Table XXXI—(See Table XVIII)

$A = 5.93$

t	$A - x$	AK
15	2.22	0.0654
21	1.50	0.0654
26	1.07	0.0659
32	0.71	0.0663
38	0.49	0.0656
50	0.20	0.0677

Average = 0.0660
$K_1 + K_2$ = 0.0661

Benzonitrile and Benzimido Ethyl Ester

Benzimido ethyl ester hydrochloride was prepared by the method described by Pinner[1] with modifications.[2] A mixture of one mole of benzonitrile and 1.25 moles of alcohol (containing not more than 0.06 per cent. water) was treated with 1.50 moles of dry hydrochloric acid gas. While the gas was being passed in, the mixture was kept in crushed ice. After standing in the cold several hours, the solution was treated with a few crystals of the benzimido ethyl ester hydrochloride to induce crystallization and allowed to stand forty-eight hours, when it became a solid mass. This was then thrown on a filter and washed with cold alcohol and ether. It was then placed in a vacuum desiccator over calcium oxide and

[1] Die Imidoäther (1892), p. 53.
[2] Marshall and Acree: THIS JOURNAL, 49, 134.

after twenty-four hours was analyzed. The yield varied from 65 to 100 per cent. The following are some typical analyses:

0.5301 gram substance gave 0.4096 gram AgCl.
0.7632 gram substance gave 0.5911 gram AgCl.
0.6166 gram substance gave 0.4777 gram AgCl.
0.6194 gram substance gave 0.4790 gram AgCl.

Per cent. chlorine,	
Found	Theoretical
19.11	19.10
19.16	.....
19.15	.....
19.12	.....

Benzimido Ethyl Ester.—As considerable difficulty was experienced in preparing pure benzimido ethyl ester by the ordinary method[1] and in keeping it pure, the following method was tried.

To an alcoholic solution of benzimido ethyl ester hydrochloride was added exactly the molecular equivalent of sodium ethylate. The sodium chloride was filtered off and the solution was distilled *in vacuo*. After several distillations a constant boiling substance was obtained, but it contained some free benzonitrile as was shown by the reaction velocity. Therefore, all solutions of the imido ester were prepared from an alcoholic solution of its hydrochloride and sodium ethylate as described under the acetimido ethyl ester.

We first proved that the free imido ester does not decompose with any appreciable velocity unless catalyzed by the ethylate. A solution of the benzimido ester hydrochloride was treated with nine-tenths of the theoretical amount of ethylate and titrated at intervals by Dr. C. N. Myers.

Time	2 hrs.	3 hrs.	22 hrs.	45 hrs.	72 hrs.	7 days	10 days	15 days	19 days
Cc. 0.2 N HCl	10.94	11.00	10.96	10.94	10.96	10.70	10.52	10.20	10.00

The amount of change due to the *uncatalyzed*, or spontaneous, decomposition of the free imido ester cannot produce any appreciable error in our constants. When portions of this

[1] Derby: THIS JOURNAL, **29**, 442 (1908).

solution were treated with N/8 sodium ethylate the imido ester was decomposed as usual.

Hydrolysis Correction.—In working with this compound hydrolysis was so marked that it was necessary to correct for it. This was accomplished in the following way: Amounts of benzimido ethyl ester hydrochloride dissolved in 10 cc. alcohol, corresponding to various stages in the reaction of a 0.25 N solution, were put in Nessler comparison tubes and diluted to 100 cc. with water, two drops of methyl orange being added to each tube. To another series of tubes containing 10 cc. alcohol, 90 cc. water and two drops of methyl orange were added 0.01 N hydrochloric acid till the colors matched those produced by hydrolysis in the first series.

The following table gives the amounts of 0.01 N hydrochloric acid necessary to produce this color:

Weight imido ester hydrochloride	Cc. of 0.01 N HCl	Corrected for blank
0.9280 g.	1.4	1.0
0.7424	1.2	0.8
0.4640	1.1	0.7
0.2774	0.8	0.4
0.1856	0.5	0.1
0.0928	0.4	0.0
0.0000	0.4	...

The following table gives corrections applied to the titrations at time periods corresponding to various values of x. These were subtracted from the values of x actually observed:

x	Correction in cc. 0.2 N HCl
0.00	0.05
2.50	0.04
6.25	0.03
8.75	0.02
10.00	0.01
12.50	0.00

Table I[1]*—0.25 N Benzonitrile, or Imido Ester, and Sodium Ethylate*

Concentration sodium ethylate	Per cent. imido ester at equilibrium	
	From nitrile	From imido ester
0.75	9.28	....
0.25	9.12	.....
0.125	9.52	....
0.125	9.60	9.44 9.12
0.0625	9.86	9.76 9.60
0.03125	9.70	9.12
0.015625	9.62	9.68

Table II—0.50 Sodium Ethylate and Benzonitrile

Concentration benzonitrile	Per cent. imido ester formed
0.5 N	7.60
0.5 N	7.72
0.375 N	8.37
0.25 N	9.06
0.125 N	11.12
0.0625 N	14.08
0.03125 N	14.10

Table III—0.25 N Benzimido Ethyl Ester and 0.125 N Sodium Ethylate

$A_1 = 12.50$	$A_2 = 0$	$K = 10.0$
t	x	K_V
41	4.82	0.0135
51	5.69	0.0136
61	6.35	0.0134
94	8.06	0.0133
119	8.93	0.0129
132	9.32	0.0130
∞	11.36	.....

Average = 0.0133
K_m = 0.1064

[1] Tables I and II are taken from another article by Marshall and Acree: THIS JOURNAL, **40**, 136, 138. The last four values for the work with the nitrile were obtained by Dr. C. N. Myers.

Table IV—0.25 N Benzimido Ethyl Ester and 0.125 N Sodium Ethylate

$A_1 = 12.50$	$A_2 = 0$	$K = 9.59$
t	x	K_V
30	3.85	0.0139
42	4.86	0.0133
51	5.54	0.0132
63	6.33	0.0130
95	8.01	0.0129
125	9.07	0.0129
156	9.82	0.0129
∞	11.32	.....

Average = 0.0132
K_n = 0.1056

Table V—0.25 N Benzimido Ethyl Ester and 0.0625 N Sodium Ethylate

$A_1 = 12.50$	$A_2 = 0$	$K = 9.25$
t	x	K_V
60	3.77	0.0677
100	5.55	0.0677
110	5.90	0.0672
125	6.42	0.0672
141	6.88	0.0668
∞	11.28	.....

Average = 0.0673
K_n = 0.1077

Table VI—0.25 N Benzimido Ethyl Ester and 0.0625 N Sodium Ethylate

$A_1 = 12.50$	$A_2 = 0$	$K = 9.42$
t	x	K_V
60	3.82	0.0686
80.5	4.73	0.0672
105	5.68	0.0666
121	6.30	0.0675
140	6.85	0.0666
162	7.43	0.0661
∞	11.30	.....

Average = 0.0671
K_n = 0.1074

Table VII—0.25 N Benzimido Ethyl Ester and 0.03125 N Sodium Ethylate

$A_1 = 12.50$	$A_2 = 0$	$K = 9.97$
t	x	K_V
72	2.56	0.00355
102	3.35	0.00343
118	3.81	0.00345
141	4.34	0.00341
170	4.97	0.00339
213	5.78	0.00334
233	6.11	0.00332
∞	11.36	.....
		Average = 0.00341
		$K_n = 0.1091$

Table VIII—0.25 N Benzimido Ethyl Ester and 0.015625 N Sodium Ethylate

$A_1 = 25.00$	$A_2 = 0$	$K = 9.33$
t	x	K_V
100	3.67	0.00177
124	4.63	0.00184
140	5.03	0.00179
160	5.55	0.00176
180	6.18	0.00177
1260	19.74	0.00164
∞	22.58	.....
Double portions used.		Average = 0.00176
		$K_n = 0.1126$

Table IX—0.25 N Benzimido Ethyl Ester and Sodium Ethylate

Concentration sodium ethylate	K_V	K_n
0.125 N	0.0133	0.1064
0.0625 N	0.00672	0.1075
0.03125 N	0.00341	0.1091
0.015625 N	0.00176	0.1126

Table X—Calculated Values of K_i and K_m

	K_i	K_m
V = 8 : 16	0.1090	0.1016
V = 8 : 32	0.1154	0.1007
V = 8 : 64	0.1193	0.0981
V = 16 : 32	0.1161	0.0989
V = 16 : 64	0.1204	0.0955
V = 32 : 64	0.1227	0.0906
Average,	0.1172	0.0976

Table XI—"K_m Found" and "K_m Calculated" for 0.25 N Benzimido Ethyl Ester and Sodium Ethylate

Concentration sodium ethylate	"K_m calculated"	K_m found"	Error in per cent.
0.125 N	0.1053	0.1064	+1.00
0.0625 N	0.1070	0.1075	+0.46
0.03125 N	0.1089	0.1091	+0.18
0.015625 N	0.1109	0.1126	+1.5
		Average error,	+0.78

These experiments show conclusively that the velocity of decomposition of benzimido ethyl ester by sodium ethylate can be expressed as a function of both the *concentration of the ethylate ions* and the *concentration of the nonionized sodium ethylate.* The two following tables show that sodium iodide produces a "salt effect" which is practically identical with that calculated in the manner described on page 379, by the use of our theory:

Table XII—0.25 N Benzimido Ethyl Ester, 0.0625 N Sodium Ethylate and 0.0625 N Sodium Iodide

A_1 = 12.50 Cor. for NH_3 = 0 A_2 = 0 K = 9.5

t	x	K_V
0	....	.....
73	4.30	0.00654
98	5.36	0.00654
121	6.16	0.00649
150	7.06	0.00652
166	7.50	0.00656
∞	11.30	

Average = 0.00653
Calculated = 0.00669

0.25 N Benzonitrile, 0.0625 N Sodium Ethylate and 0.0625 N Sodium Iodide.—Ten cc. required 3.12 cc. 0.2 N hydrochloric acid at first and 4.22, 4.23, 4.23 cc. at equilibrium. This corresponds to 8.8 per cent. imido ester present at equilibrium.

Table XIII—0.25 N Benzimido Ethyl Ester, 0.125 N Sodium Ethylate and 0.125 N Sodium Iodide

$A_1 = 12.41$ Cor. for $NH_3 = 0.09$ $A_2 = 0$ $K = 12.05$

t	x	K_V
40	4.63	0.0129
55	5.79	0.0128
77	7.06	0.0124
100	8.12	0.0123
110	8.71	0.0129
124	8.97	0.0125
∞	11.46	.....

Average = 0.0127
Calculated = 0.0131

0.25 N Benzonitrile, 0.125 N Sodium Ethylate and 0.125 N Sodium Iodide.—Ten cc. required 6.29 cc. 0.2 N hydrochloric acid at first and 7.41, 7.38, 7.39 cc. at equilibrium. This corresponds to 9.0 per cent. imido ester present at equilibrium.

CONCLUSIONS

The experimental work and theoretical discussion in the preceding pages show that ethylates accelerate in a *purely catalytic* way the decomposition of imido esters into nitriles and alcohols and the addition of alcohols to nitriles; the velocity of the noncatalyzed reaction is so small that it can be entirely neglected. By a comparison of the reaction velocities and the conductivity data it is seen that the ethylate ions have a definite influence on the reaction which is a simple function of their concentration. The nonionized sodium ethylate, furthermore, has a definite effect on the reaction velocity which can be expressed as a simple function of the concentration of the molecules. We refer all data to the normal solution and use the expression K_i for the effect of a gram equivalent of the ethylate ions, and the expression K_m for the quantitative

action of a gram equivalent of the sodium ethylate molecules, and find practically constant values for K_i and K_m, whatever the concentration of the ethylate. For benzonitrile and benzimido ethyl ester the value $K_i : K_m = 0.1172 : 0.0976$ was found, while for acetonitrile and acetimido ethyl ester the values $K_i : K_m = 0.344 : 0.228$ were obtained.

This work proves that the purely catalytic action of sodium ethylate on the decomposition of imido esters is exactly analogous to the reaction of alkyl halides with sodium, potassium and lithium ethylates, with sodium, potassium and lithium phenolates, and with sodium 1-phenyl-3-thiourazole. In all of these cases the velocity of the reaction can be expressed as a function of the concentration of the ions increased by a function of the concentration of the nonionized molecules.

The important "salt effect," noted in so many reactions when salts are added, has been studied in all of the cases discussed and proved to be due *chiefly* to a change of the concentrations of the ions and molecules demanded by the Arrhenius theory of isohydric solutions. Small subsidiary effects may be due to the greater or smaller reactivity of double compounds formed, and to physical changes in the solution, such as variations in viscosity, double salts, ionization and electronic phenomena.

The investigation is being continued to learn if the same value for K_i is obtained by the use of potassium and lithium ethylates. The important subject of "salt catalysis" is one of the chief objects of these researches.

JOHNS HOPKINS UNIVERSITY
June 1, 1912

CORRECTION

In recent communications upon the relation between ionization and chemical action, under the influence of α-rays, the values given for N, the total number of ions (estimated from the data of Geiger[1], should refer to *pairs of ions*. This correction does not affect any of the general conclusions as to the equivalence of ionization to molecular action, but does necessitate a modification of the proposed mechanism of ozone

[1] P. Roy. Soc., **82**, A, 486.

formation so as to fit four instead of two ions per molecule of ozone, which change would bring ozonization into agreement with the provisions of electrolysis. This correction applies throughout my papers on ozone formation[1] and also to those upon other reactions in gaseous and liquid systems.[2]

S. C. LIND

REPORT

THE BROWNIAN MOVEMENT AND THE SIZE OF THE MOLECULES[3]

Every day we see liquids in equilibrium, and all parts of them seem to us to be motionless. If we put a denser object into them it falls, perfectly vertically if it is spherical. Finally, when it has reached the bottom of the vessel, we know that it will not rise of its own accord.

These are very familiar ideas, and yet they hold good only for the dimensions to which our organs are accustomed. It is only necessary to examine with the microscope little particles placed in water to see that each of them, instead of falling regularly, is animated by a quite irregular and very brisk motion. They come and go, wheel round, rise, fall, and again ascend without showing any tendency to rest. This is the *Brownian movement*, named after one of your fellow-countrymen, the botanist Brown, who discovered it in 1827.

This remarkable discovery attracted very little attention. The physicists who heard tell of this agitation compared it, I think, to the movement of dust which one sees with the naked eye in a ray of sunlight, the effect of air currents caused by slight inequalities in the temperature or pressure. But in this case neighboring particles move nearly in the same direction, and roughly indicate the form of these air currents. You will see, on the contrary, that the Brownian movement of two particles is completely independent, even when the distance between them is less than their diameter.

I am going to try to show you this phenomenon, one of the most beautiful which has been revealed to us by the microscope, and one which shall prove to be a faithful picture of the movement of the molecules, or, rather, we shall prove that *it is itself a molecular movement* (just as the infrared radiations are actually light).

[1] Le Radium, **9**, 104; Monats. Chem., **32**, 295; THIS JOURNAL, **47**, 397.

[2] Le Radium, **9**, 426; J. Phys. Chem., **16**, 564; Trans. Am. Electrochem. Soc., **21**, 177.

[3] Address delivered before the Royal Institution, February 24, 1911, by Professor Jean Perrin, Faculté des Sciences à la Sorbonne, Paris, and printed in the Chem. News, **103**, 189, 203, 215.

You see here on the screen a cinematograph reproduction of the movement in water of round grains of gamboge (diameter rather less than 0.001 mm.). This film was prepared by MM. Victor Henri and Comandon (Pathé film), and was kindly lent me by them. I should prefer to show you the emulsion directly, by projecting on the screen the animated view which the microscope gives of it, but the enlargement necessary would be so great that the luminosity of the projection would be too faint for this large amphitheater.

You see that in this very irregular movement it is not possible to pick out any general current drawing along several particles simultaneously. The movement cannot therefore be due to shakings of the plate which carries the droplet which is being watched, for those trepidations, when they are intentionally caused, produce precisely such currents which one sees simply superposed on the irregular agitation of the granules. Moreover, the Brownian movement persists on a thoroughly rigid structure, by night in the country as decidedly as by day in the town, on a table ceaselessly shaken by the passing of heavy vehicles (Gouy). There is not even any necessity to trouble to make the temperature of the droplet uniform. All that is gained by so doing is the suppression of currents which are perfectly recognizable, and have no relation to the irregular agitation observed. Nothing is gained either by greatly diminishing the intensity of the illuminating light or by changing its color (Gouy).

Of course, the phenomenon is not peculiar to water, but occurs in all fluids, being more marked when the fluids are less viscous, and hence especially strong in gases. In a moment I will show you the film of granules of gamboge in water; here is another which I owe to the kindness of MM. Victor Henri and de Broglie, and which shows you the Brownian movement in air of the ultramicroscopic droplets which form tobacco smoke.

In a given fluid the magnitude of the granules makes a great difference, and the agitation is the more marked the smaller the granules. This property was mentioned by Brown when he first made his discovery. As to the nature of the granules, it appears to have little if any influence. In the same fluid two granules move in the same way when they are of the same size, whatever their substance and density (Jevons, 1869). And, incidentally, this absence of influence of the nature of the granules eliminates all analogy with the displacements which a morsel of camphor undergoes when thrown on water.

Finally—and perhaps this is the strangest and most truly novel property—the Brownian movement never stops. In-

side a cell, closed so as to prevent evaporation, it can be watched for days, months, and years. It is exhibited by the liquids enclosed in quartz for thousands of years. *It is eternal and spontaneous.*

All these characteristics point to the conclusion that the granules only reveal an agitation peculiar to the fluid itself, which they do more readily the smaller they are (just as a small boat more readily feels the waves of the sea than a large one). Thus we arrive at an essential property of what is called a fluid in equilibrium; this apparent rest is only an illusion due to the imperfection of our senses, and in reality corresponds to a definite permanent regime of violent and spontaneous agitation.

I should like to tell you how this perpetual agitation derives from the second law of thermodynamics the rank of an absolute truth (Gouy, 1888), and reduces it to a law of statistics, *i. e.*, to the affirmation of probabilities which are feebler the smaller the system to which one applies them, but our time is too short, and I must at once pass to the discussion of the cause within the fluid by which the phenomenon can be explained.

To find this cause we must appeal to molecular hypotheses. You know how ancient they are, for Democritus and Leucippus, more than twenty centuries ago, knew that matter is composed of indestructible granules in incessant movement, atoms which Chance or Destiny grouped in the course of ages into the forms and substances with which we are familiar. But only tradition tells us of these early theories, and in the beautiful poem, written long after, in which Lucretius describes the atomistic views of Epicurus, I see nothing to show how these Greek philosophers were led to attribute a granular structure to matter.

It seems to me that the hypothesis might have been suggested to them by the familiar properties of mixtures. In any case there is a really serious argument in these properties which I will first discuss. For example, we all say when we have dissolved sugar in water that the sugar and water exist in the mixture, although we cannot distinguish different parts in the sweetened water. Similarly, we say that there is oxygen in the air, and, more generally, we often recognize without hesitation in the properties of a mixture those of its constituents.

This is easily understood if the substances which form the mixture subsist in it, as flowers of sulphur and iron filings exist side by side in this mixture which I am making before your eyes. You can no longer distinguish the yellow from the black grains, and the whole looks to you to have a homogeneous

gray color. You will recognize the iron, however, even from some distance, if I bring a magnet near the vessel containing the mixture; and this does not surprise you, for you know that you need only come nearer in order to distinguish the grains of sulphur from those of iron, which are in juxtaposition but are unchanged. Similarly the persistence of the properties of sugar in sweetened water would easily be explained if in this solution there are present little particles, simply mixed in juxtaposition, which by themselves would make water, and other particles which alone would form sugar. These elementary particles, or *molecules*, would be found in all mixtures in which we could detect sugar and water, and only their extreme minuteness would prevent us from seeing them individually.

Moreover, the molecules of a pure substance like water, if they exist, must be identical, otherwise they would not behave similarly when subjected to different attempts at fractionation, by boiling, for example, and the fractions successively separated would not be identical, whereas as a matter of fact they are (Dalton).

If the molecules exist, in order to understand solution and diffusion, we are forced to admit that they are in ceaseless motion. Suppose we pour alcohol carefully on to water, or superpose carbon dioxide and hydrogen (Berthollet), and leave the system at a perfectly constant temperature. You know that the two fluids gradually interpenetrate one another although the lighter may be above, and this could not occur if their molecules were motionless. When we have thus seen that the molecules of carbon dioxide diffuse into hydrogen, into oxygen, into nitrogen, and so on, it seems probable to us that they would also diffuse into carbon dioxide itself, and this amounts to saying that the molecules of carbon dioxide are in incessant motion.

This movement of the molecules also explains the pressure exercised by fluids on the walls of containing vessels, the pressure being due to the bombardment of the molecules against the walls. This explanation, worked out in the eighteenth century by Euler and Bernouilli, leads to Boyle's law, and enables us to calculate the mean velocity of the molecules of different gases (in the air of this room, for example, the molecules would have a mean velocity of about 500 meters per second). This result signalizes the first success, in modern physics, of the old hypothesis of Greek atomism.

But we are still far from a direct verification, and the supposed movements of the molecules escape us, just as the movements of the waves of the sea escape an observer who is too far away to see them. However, if a boat were in view the

same observer might see a rocking which would reveal to him the agitation of which he had no suspicion. Might not one hope similarly that if microscopic particles were present in a fluid these particles or this dust, if they were large enough to be watched under the microscope, might also be small enough to be appreciably affected by the blows of the molecules?

Now you will guess what explanation we are going to give to the Brownian movement. Every granule situated in a fluid is unceasingly struck by the molecules round it. There is no chance that these blows will exactly balance one another; our granule will thus be irregularly tossed about, and perhaps this is the Brownian movement.

This tempting explanation (Weiner, 1863) was long regarded as doubtful. In order that it may be accepted it is at least necessary that the theory should foretell the order of magnitude of the phenomenon, and as yet we do not know whether it is not immeasurably greater (or less) than our hypothesis permits.

We shall see that this quantitative verification is possible, but to arrive at it I must remind you how, some time ago, the measurement of the viscosity of gases enabled us to determine the probable size and weight of the molecules. I shall then show you that the Brownian movement, supposed to be due to the blows of the molecules, also gives a means of determining the size of the molecules. If the two results obtained by such very different methods agree, the origin of the Brownian movement will be determined.

If we admit the existence of the molecules, we are forced, in order to explain the chemical laws of discontinuity (Law of Definite Proportions, Law of Multiple Proportions, Law of Proportional Numbers), to admit with Dalton the existence of *atoms*, characteristic of the various simple substances. For then the composition of a molecule necessarily varies by discontinuous bounds, corresponding to the entrance (or departure) of at least one atom. Thus we could deduce with precision, from the phenomena of chemical *substitution*, not the absolute weights of the molecules and atoms, but the ratios of these weights.

When, for instance, calcium is dissolved in water only half the hydrogen of the water is displaced. This may be explained by assuming that the hydrogen of each molecule of water is composed of two equal parts. These parts must be indivisible by all chemical means, since no other substitution ever gives us reasons for thinking that there are more than two; these parts are called "atoms" of hydrogen. Moreover,

a molecule of water, like any mass of water, weighs nine times as much as the hydrogen it contains; thus it weighs eighteen times as much as a single atom of hydrogen. By similar reasoning it is found that a molecule of benzene weighs seventy-eight times as much as one atom of hydrogen. The weights of the molecules of benzene and of water and of the atom of hydrogen are thus in the proportion of 78 : 18 : 1. Similarly, in many cases the ratios of the weights of different molecules and atoms may be found. (Strictly speaking, all these ratios are not yet known; for instance, there is no substitution which gives the molecular weight of a simple substance like oxygen. We shall see in a moment how Avogadro's law enables us to fill up this gap.) It is very remarkable that all these determinations are concordant, so that, for example, we can mention thousands of substances from the study of which we can deduce that the atom of carbon is twelve times as heavy as the atom of hydrogen. This gives us confidence in the atomic theory, but tells us absolutely nothing about the scale of the sizes of the molecules, whether near us or infinitely distant.

We see at least that in order to arrive at the absolute weights of the different atoms or molecules, it is only necessary to know one of them. At the same time we should also get (as Helmholtz has shown) the elementary charge which one atom of hydrogen (or, more generally, one monovalent ion) transports in electrolysis. For if we knew the weight of one atom of hydrogen, we should know how many of these atoms one gram of hydrogen contains, and hence how much each carries in electrolysis, for we know that one gram of hydrogen transports about 10,000 coulombs.

Let us then try to find one of these elementary weights, that of the molecule of oxygen, for instance.

Kinetic Theory.—Suppose that a mass of oxygen occupying 1 liter (at ordinary temperature and pressure) is liquefied. The n molecules which are present in it will almost come into contact, for the liquid is nearly incompressible. Now, we know that the true volume of the granules of a heap of sand is approximately two-thirds of the apparent volume of the heap; it is therefore probable that the true volume of our n molecules is not much less than two-thirds of the volume of the liquid, and if this value is accepted there can be no very great error. A more exact theory, due to van der Waals, leads us to assume a value twice as small and to write: $n \times$ *volume of 1 molecule* $= 1/3$ *volume of the liquid.*

On the other hand, in the gaseous state in a given volume a fixed number of molecules n collide more often the larger

they are. Or, if you prefer it, the mean free path of the molecule L is smaller in proportion as the molecules are larger or have a larger surface. Clausius and Maxwell have calculated this relation (assuming that the molecules are spherical) and have found $n \times$ *surface of 1 molecule* $= 0.7 \times$ *volume of gas/ mean free path.*

If we know the mean free path we should then have, by dividing the two equations by one another, the ratio of the volume $4\pi R^3/3$ to the surface $4\pi R^2$, i. e., the radius of the molecule, and hence its volume and surface. One of these two equations, the first, for instance, would give us n, the number of molecules which form a known mass of oxygen. The mass of the molecule of oxygen will thus be obtained.

But for this we must know the free path of the molecule. Maxwell was able to deduce it from the force which is exerted by friction between two gaseous layers which slide one on the other with different velocities.

It is easy to show the existence of this "internal friction" or "viscosity." You see the jet of gas which I light at the end of this long capillary tube. If now I shorten the tube (by cutting it) the jet of gas coming from it gives a much longer flame. Thus the gas comes out more quickly from a tube of the same section. There was, therefore, a large amount of friction in the path which I have cut off, in the interior of which the cylindrical gas columns slide on one another.

The molecular hypothesis easily explains this friction. In order to understand it let us imagine two trains of passengers moving on parallel rails with almost equal velocities. The passengers could amuse themselves by jumping incessantly from one to the other, receiving a slight shock every time. Thanks to these shocks the passengers alighting on the slower train would slowly increase its velocity, while in the same way that of the quicker train would slowly decrease. The two velocities would thus be equalized as by friction if the constant difference were not maintained. The same argument applies to two gaseous layers sliding one on the other, since they bombard each other without ceasing by a transference of the molecules from one to the other.

The mathematical analysis of this simple conception, made by Maxwell, has shown that the force of friction per square cm. between two gaseous layers at a distance of 1 cm., having a relative velocity of 1 cm. per second (a force which explains viscosity), approximately satisfies the equation: *viscosity* $=$ *1/3 density* $\times$ *free path* $\times$ *molecular velocity.*

The density of the gas and the viscosity are measurable. If we can determine the molecular velocity (mean) we shall have the free path.

This last process is easy. The pressure of the gas, as we have already said, is explained by the continual bombardment of the molecules on the walls, and these shocks are the more effectual the heavier and more rapid each of them is. The exact expression, due to Bernouilli, gives: *pressure* = *1/3 density* × *square of molecular velocity*. This gives the required velocity. Applied to oxygen we find about 500 meters per second at the ordinary temperature; the molecules we are breathing are moving as rapidly as bullets.

We have now only to proceed step by step; we shall have the mean free path (0.0001 mm. for air in ordinary conditions), then the molecular diameter (a molecule of oxygen is to a man very nearly as a man to the sun), then the number of molecules n to a liter (about 30,000 millions of billions), and finally the weight of the molecule of oxygen which will give us, as we have seen, all the other weights of molecules or atoms.

We find thus, the possible error being roughly 30 per cent., that the weight of 1 atom of hydrogen is only the billion-billionth part of 1.6 grams, or 1.6×10^{-24} gram. As to the elementary charge, it will be about 5×10^{-10}, or about the thousand-millionth of the charge which can be detected by an ordinary electroscope.

I am now going to tell you how, thanks to the Brownian movement, I have been able to give other means of obtaining the sizes of the molecules.

Law of Avogadro.—I have just shown you how the study of chemical substitution gives, for example, the ratio of the masses of the molecules of benzene and water, which ought to be to one another as 78 : 18. Two masses of benzene and water which are in the ration of 78 : 18 each contain the same number of molecules. Now, if we measure the volumes occupied in the gaseous state by these two masses, at the same temperature and pressure, we find that these two volumes are equal. This is not chance, and one invariably finds that two gaseous masses which contain the same number of molecules occupy the same volume when they have the same temperature and pressure. This is Avogadro's law, which may be stated as follows:

"In the gaseous state equal numbers of molecules of different substances, contained in equal volumes at the same temperature, produce in it the same pressures."[1]

[1] Avogadro's law, once well established, will give us by extrapolation molecular weights not obtained by the methods of chemical substitutions. For example, when we have found that 32 parts of oxygen or 2 parts of hydrogen produce in the same volume and at the same temperature the same pressure as 18 parts of water vapor, we know that the masses of these three kinds of molecules are to one another as 32 : 2 : 18.

You have learned elsewhere (Boyle's law) that the pressure thus developed varies inversely as the volume occupied.

These gas laws have been extended by van't Hoff to dilute solutions. We must, of course, in that case consider, not the total pressure exerted on the walls, but only that part of that pressure which is due to the blows of the dissolved molecules, the part called the osmotic pressure of the dissolved substance (which can be measured only by means of a "semi-permeable" wall, which stops the molecules of the solute but not those of the solvent). The laws of Avogadro and Boyle thus become:

"In the dilute state (gaseous or dissolved) equal numbers of any molecules whatever, contained in equal volumes at the same temperature, produce in them the same pressure. This pressure varies inversely as the volume occupied."

These laws are applicable equally to all molecules, large or small. The heavy molecules of sugar or of sulphate of quinine produce neither greater nor less effect than the molecule of hydrogen. Yet the molecule of sugar contains 45 atoms, and that of sulphate of quinine more than 100, and it would be easy to find other more complex molecules which obey the laws of van't Hoff (or those of Raoult which follow from them).

Is it not then conceivable that there is no limit of size for the assemblage of atoms which obeys these laws; is it not conceivable that even visible dust also obeys them exactly, so that a granule agitated by the Brownian movement has neither more nor less effect than a molecule of hydrogen, as regards the action of its bombardments on a wall which stops it? Or, more briefly, is it unreasonable to think that the laws of perfect gases may be applied also to emulsions composed of visible grains?

I have made this assumption, and it is in this direction that I have sought a crucial experiment which would decide the origin of the Brownian movement, and at the same time would either provide or preclude an experimental basis for the molecular theories.

The following appears to me to be the simplest:

The Distribution of Equilibrium in a Vertical Column of Diluted Matter.—You know that the air is more rarefied on mountains than at sea level, and that in a general way a column of gas is compressed under its own weight, the state of equilibrium resulting from the conflict between the force of gravity, which makes the molecules fall, and their movement, which scatters them incessantly.

The law of rarefaction formulated by Laplace (to show how the altitude can be deduced from the barometer) follows of

necessity from Boyle's law, and can be enunciated as follows:

Every time that one ascends a fixed distance, the density is divided by the same number. Or, more briefly, equal vertical elevations are accompanied by equal rarefactions.

For example, in air at the ordinary temperature the density diminishes by one-half each time one ascends 6 kilometers (it is immaterial from what level).

But the elevation which produces a double rarefaction would not be the same in hydrogen. A simple process of reasoning shows that the way in which the nature of the gas influences the result is a necessary consequence of Avogadro's law, and may be enunciated as follows:

The elevations which produce the same rarefaction for two different gases (at the same temperature) are inversely proportional to the weights of the molecules of these gases.

For instance, if in oxygen at 0° it is necessary to rise 5 km. to make the density twice as small, it would be necessary to rise 80 km. in hydrogen at 0°, since the molecule of hydrogen is 16 times as light as the molecules of oxygen.

You see here a diagram showing three huge vertical cylinders (the largest is 300 km. high) into which the same number of molecules of hydrogen, helium and oxygen have been placed. At a supposed uniform temperature, the molecules would distribute themselves as the diagram shows, collecting more towards the bottom the heavier they are.

Now we have been led to believe that the laws of perfect gases are possibly applicable to emulsions. If this is so, and if we make an emulsion in which the grains are equal, the distribution of matter in a vertical column of this emulsion ought to be the same as in a gas. In other words, once arrive at the distribution of equilibrium and then equal elevations will be accompanied by equal rarefactions. But if it is necessary to rise only 0.05 mm., i. e., 100 million times less than in oxygen, for the concentration to become twice as small, then we must conclude that each grain of the emulsion weighs 100 million times more than one molecule of oxygen. This last weight could be ascertained if we could weigh the grain, which would be a stage between the molecular dimensions and those which are in our scale.

Of course the effectual weight of this grain would be the difference between its real weight and the thrust it would undergo in the liquid (according to Archimedes' principle). If the granules were lighter than the intergranular liquid, they would accumulate in the upper layers (equal depressions would produce equal rarefactions). They would distribute

themselves uniformly if they had the same density as the liquid.

Practical Realization.—To test these results I used the emulsions which are obtained by precipitating alcoholic solutions of resins with water. Thus, as you see, we get with gamboge a beautiful yellow liquid, with mastic a white liquid like milk. The microscope reveals in these liquids the resin precipitated in the form of *solid* round granules, which do not agglutinate when the chances of the Brownian movement bring them into contact (which is what happens with other resins which give soft granules).

But the diameters of these granules are very varied, and I had to sort them so as to get emulsions in which all the grains were nearly the same size. The method I employed may be compared to the fractionation of a liquid mixture by distillation. Just as during distillation, the parts first vaporized are relatively richer in volatile constituents, so during the centrifugation of an emulsion the portions first deposited are relatively richer in large granules. Thus you will see that it is easy to find a practical method of sorting the grains according to their size by fractional centrifugation. The operation is long (I spent some months over it), but it only requires patience.

Once get an emulsion with sufficiently uniform granules, and then the mean weight of the granules must be determined. Their density is measured like that of any other powder (the weight of resin in suspension in the flask used is determined by simply drying). The only difficulty is then to determine the diameter. The obvious way seems to be to measure it with a microscope by the clear chamber method by means of a micrometer objective. But the granules used are so small that errors of 20 per cent. or more might easily be made. A method which is almost as direct consists in allowing a droplet of the emulsion to evaporate on the micrometer objective; it is found, as you can see here on a projection, that the granules then arrange themselves in regular lines, the length of which could be measured with a fair degree of accuracy. Dividing this length by the number of granules gives the diameter.

Another long but more accurate method consists in counting how many granules there are in a known volume of the standardized emulsion, which gives the mass of a granule, and hence its radius, since we know the density. For this method I used the fact, accidentally observed, that in a feebly acid medium the grains of gamboge adhere to the glass. At an appreciable distance from the walls the Brownian movement is not modified, but as soon as the chances of this movement bring a grain into contact with a wall, the gran becomes motionless.

The emulsion thus gets progressively weaker, and after some hours all the granules it contained are fixed. One can then count at one's leisure all those which come from a cylinder of arbitrary base (measured by the clear chamber).

Finally, a third method, which I shall not explain to you in detail, is based on the observation of the time necessary for the upper portion of a vertical column of emulsion (several cm. high) to clarify to a given height. This time, required by the granules to descend on the average from this height, gives the diameter by applying the law of the fall of a sphere in a viscous fluid (Stokes).

These three processes agree, and this must be so to give us confidence in the accuracy of the measurements of a radius which is less than a thousandth of a mm.

Method of Observation.—We must now get an arrangement which will enable us to ascertain the distribution of equilibrium as a function of the height. For this purpose a drop of emulsion is placed in a shallow tank, the depth of which is 0.1 mm.; the drop is at once flattened out by a cover slip which closes the tank and the edges of which are paraffined to prevent evaporation.

The tank can be arranged vertically, the body of the microscope being horizontal, and thus the vertical column throughout which the emulsion can distribute itself may be made some mm. high. It will be seen that the grains accumulate in the lower layers, and tend to give rise to a distribution of equilibrium (practically reached after one or two days), in which the progressive rarefaction as a function of the height is manifested as you can see in the projection, which plainly recalls the law of rarefaction of heavy gases.

But however small our granules are, they are so heavy that the rarefaction is very rapid, and the height over which measurements can usefully be made is less than 0.1 mm.

The tank can also be made horizontal, the body of the microscope being vertical, in which case only about a quarter of an hour is necessary for equilibrium to be established. The objective of the microscope, of great enlarging power, has only a small depth of field, and we can only see clearly, at the same instant, the granules situated in a very thin horizontal layer, the thickness of which is only a little over 0.001 mm. If the microscope is raised or lowered one sees the granules of another layer. The distance between these two layers may be deduced from the vertical displacement read on the screw of the microscope; the ratio of the number of granules perceived gives the rarefaction corresponding to a known elevation. It was with this apparatus that I made my first experiments.

I was not sure that there would be the least rarefaction, and moreover, not even sure whether, on the contrary, all the granules would not group themselves quite against the bottom. But I saw that a permanent state of uniform rarefaction was established. This rarefaction is specially striking when, keeping the eye fixed on the preparation, the observer rapidly raises the microscope by means of its micrometer screw. The granules are then seen to be rapidly rarefied, like the atmosphere round an aerostat which is rising.

It now remains to make accurate measurements. When one sees in the field some hundreds of granules which are moving in all directions or which disappear while new ones make their appearance, one soon gives up trying to count them. Luckily we can take instantaneous photographs of the different layers, and then at our leisure count the number of granules in these layers on the plates.

It is thus easy to verify that equal elevations are accompanied by equal rarefactions. For instance, for granules of radius equal to 0.212μ three successive rises of 30μ practically lower the concentration to one-half, one-quarter and one-eighth of its value. With other grains of radius equal to 0.367μ an elevation of 6μ is enough to make the density about twice as small.

To obtain the same rarefaction in air we have seen that it would be necessary to rise 6 km., a thousand million times as much. If our theory is correct, the weight of a molecule of air would be the thousand-millionth part of the weight of one of our granules in water. The weight of the atom of hydrogen would be obtained in the same way, and now our interest centers on finding out if we shall thus obtain the same numbers as those given by the kinetic theory.

So I was much elated when I found at the first attempt numbers which were the same as those obtained by the kinetic theory, i. e., by a fundamentally different method. I also varied the conditions of the experiment as much as I could. For instance, the mass of my granules had a series of values ranging between limits which were to one another as 1 : 40; I changed the nature of the granules, using different resins (especially mastic); by the addition of glycerol I increased the viscosity of the intergranular liquid in the ratio of 120 : 1, at the same time changing the nature of the liquid; finally, I made a considerable change in the apparent density of the granules, which, in water, varied from the same to five times as much, and which became negative for gamboge in glycerol

with 10 per cent. of water (in this last case the granules being lighter than the liquid accumulated in the upper layers).[1]

I always obtained concordant results, giving for the atom of hydrogen a weight very nearly equal to the value 1.6×10^{-24}, given by the kinetic theory.

I do not think this agreement can leave any doubt as to the origin of the Brownian movement. To understand how striking it is it must be remembered that before the experiment one could not have dared to affirm that the fall of concentration would not be negligible for such a small height as a few microns, or that all the granules would not collect in the immediate neighborhood of the bottom of the tank. The first eventuality would give a zero value, and the second an infinite value for the weight of the hydrogen atom. That one should have hit exactly upon a value so close to that foretold, with *each* emulsion, in the *enormous* interval which seems *a priori* possible, could obviously not be a chance coincidence.

But there is more to be said. While the kinetic theory, because of the simplifications permissible in its calculation, gives results of an uncertain degree of approximation, even from perfect experiments, the numbers given by emulsions correspond to a true measure, such that there is no limit to its accuracy. By this method we can readily weigh the atoms, and not only roughly estimate their weight.

The two series of experiments which I regard as the most accurate have thus given me for the weight of the atom of hydrogen (after the enumeration of about 30,000 granules) the value $1.47/1{,}000{,}000{,}000{,}000{,}000{,}000{,}000{,}000$, or more briefly 1.47×10^{-24} grams.

The sizes of the other molecules can be derived from this. For example, you will easily see that there must be in each cc. of air (in normal conditions) thirty-one thousand millions of thousand millions of molecules, and that the elementary charge or electron must be 4.2×10^{-10} (C. G. S. electrostatic units).

The Sizes of the Molecules can be Deduced from the Degree of Agitation.—Thus we have extended the laws to emulsions with much success, and at the same time obtained the absolute weights of the atoms. It is remarkable that in these measurements we have not had to concern ourselves about the activity of the Brownian movement. The laws of gases are verified by emulsions equally well in glycerol, in which the Brownian movement is hardly perceptible, and in water, in which

[1] Quite recently, under my direction, M. Bruhat made the temperature vary from —10° to +58°, and still found the same weight.

it is very brisk, the only difference being that the distribution of equilibrium occurs much more quickly in water than in glycerol.

On the other hand, this Brownian movement, when studied by itself, will give us a new method of determining the size of the molecules, perhaps less intuitive than the preceding method, but just as accurate; it was suggested by Einstein in an admirable theoretical article (1905).

Without trying to follow the infinitely complicated path which a granule describes in a given time, Einstein considers only its displacement during that time, i. e., the rectilineal segment which joins its starting point to its final position, and shows that if certain fundamental hypotheses of the kinetic theory are correct, the knowledge of the *mean* value of this displacement enables us to determine the sizes of the molecules.

I cannot now give the details of this argument, and must confine myself to saying that the principal hypothesis used by Einstein consists in supposing not only, as has already been done, that at the same temperature all the molecules have the same mean energy of movement, but that even a perceptible granule has the same mean energy of movement. Then Einstein's formula gives this mean molecular energy, since we know the mean displacement in a given time, in a liquid having a known viscosity, of spherical granules of known radius. The molecular energy can be obtained thus, and at the same time the masses of the different molecules, for we have seen that we know what must have been their velocities in order that their bombardments on the walls might explain the pressures observed.

Einstein pointed out that the order of magnitude of the displacements observed agreed perfectly with the theory, and left to the experimenters the task of making a more precise comparison. Since I had rough granules of known diameter, I was in a position to make this comparison, as M. Langevin pointed out to me when he told me of Einstein's theory, of which I was then ignorant. I first entrusted the measurements with gamboge to M. Chaudesaignes and with mastic to M. Dabrowski, and then I myself plotted the positions. The result was decisive and showed the rigorous exactitude of Einstein's formula, the weight of the atom of hydrogen calculated by this method being 1.45×10^{-24} gram, practically identical with the number which the distribution in height of the emulsions gave me.

You see on the screen here, enlarged so that sixteen divisions represent 50 microns, three diagrams obtained by trac-

ing the segments which join the consecutive positions of a single granule of mastic of radius 0.52μ, marked at intervals of 30 seconds, with a clear chamber. It was by taking the mean of similar segments that Einstein's formula was verified.

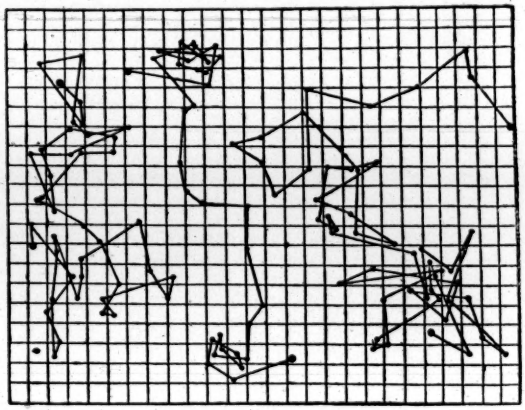

Fig. 1

These diagrams, however, give you only a very feeble idea of the enormous complexity of the actual trajectory. If, for instance, the positions were plotted at the end of each second, each of these rectilineal segments would be replaced by a polygon of thirty sides, relatively just as complicated as the diagram here reproduced, and so on.

To vary these conditions I succeeded in preparing granules much larger than those which I had used up to the present. For that purpose I allowed water to fall slowly on an alcoholic solution of mastic, by a funnel with a drawn-out tube. The granules which are formed in the zone of passage have usually a diameter of a dozen microns, a diameter which is measured directly in the clear chamber, and they are then about 100,000 times heavier than the smallest I used. In order that this weight should not keep them constantly in immediate contact with the bottom, I observed them in a solution of urea which has almost the same density as theirs. I have thus shown that Einstein's formula is still applicable. Finally, I proved

another formula, also deducted by Einstein from the molecular hypotheses, which relates to the mean rotation of a granule in a given time. This formula foretelling about 100° of rotation per second for granules of the order of a micron would appear to be difficult to verify. But, luckily, I had large granules; owing to the size of these grains, and because some of them contained little enclosures which act as marks, *I have been able to demonstrate and measure their rotation.* The measurements, as yet not very accurate, gave me 1.56×10^{-24} as the weight of the atom of hydrogen, so that there is no doubt about the applicability of this new method of arriving at the size of the molecules.

I have nothing more to tell you about my researches, but you will at least allow me to mention other quite recent methods, which also enable us to determine the sizes of the molecules. One of them, due to Lord Rayleigh, gives the number of molecules contained in a column of air of calculable mass, from the diffraction which they cause in solar light, and which, favoring the most refrangible colors, is the origin of the *blue of the sky.*

To determine the size of the molecules it is thus only necessary to measure at the same time, for the same radiation, the light of the sun and in a known direction that of the sky. The measurements (Bauer and Moulin), which do not allow of great accuracy, because of the difficulty of calculating the part which the rays reflected from the ground take in the illumination of the sky, nevertheless give the order of magnitude very fairly, indicating within about 50 per cent. 1.6×10^{-24} for the weight of the atom of hydrogen.

Another more accurate method is based upon the measurement of the electric charges transported by microscopic droplets. These charges are generally small, and are integral multiples of an atom of electricity, thus directly measurable, which is equal to that which an atom of hydrogen can transport in electrolysis. As the amount transported by 1 gram of hydrogen is known, we have thus the weight of the atom. This method, suggested by Townsend and Sir J. J. Thomson, and perfected by H. A. Wilson, and especially by Millikan (who succeeded in proving very definitely the atomistic structure of electricity), actually gives numbers lying between 1.4×10^{-24} and 1.7×10^{-24}.

Another group of measurements has its origin in the properties of radioactive substances. You know that some substances emit α rays which make zinc sulphide phosphoresce. Sir William Crookes, examining this phosphorescence under the microscope, saw that it resolved itself into a swarm of

scintillations extinguished as soon as they appeared. The rays which excite them are material, for wherever they penetrate the presence of helium may be proven (Rutherford); they are probably formed by atoms of helium positively charged. Sir William Crookes supposed that each scintillation marked the arrest of one of these atoms, which are hurled out with the enormous velocity of 20,000 km. per second. If then the number of scintillations due in a given time to a known mass of radioactive substances is counted, and if we measure the volume of helium liberated in the same time, we know how many atoms this volume contains, and the size of the molecules follows from it. We can also (I do not lay stress on this point, simply for want of time) measure the positive charge radiated or the fraction of the radioactive substance destroyed. These wonderful experiments give for the weight of the atom of hydrogen numbers lying between 1.4×10^{-24} and 1.6×10^{-24}.

I can only mention to you the existence of the beautiful theories by which Planck and Lorentz have connected the size of the molecules with the distribution of energy in a spectrum of an incandescent substance. The measurements, which may be made very accurate, now give for hydrogen the weight 1.6×10^{-24}.

I think you will be struck by the diversity of the ways which thus lead to the same result. If our hypotheses are false, each of these phenomena could give any range of values lying between zero and infinity. For instance, as regards the Brownian movement, the measurement of the mean displacement would give numbers differing for large and small granules. These values would, moreover, bear no relation to those, equally variable, given by the distributions in height. The fact that there is convergence, not only in each method, but in all the methods, that phenomena as fundamentally different as the viscosity of gases, the Brownian movement, the blueness of the sky, the electrification of droplets, radioactivity, the distribution of energy in the spectrum, all show the discontinuity of matter, and give the same magnitudes for the elements of matter, *these facts demonstrate the objective reality of the molecules*. Perhaps you will also find that this marvelous agreement gives you a good example of the satisfaction that the love of the beautiful finds in the study of the sciences.

JACOBUS HENRICUS VAN'T HOFF. Sein Leben und Wirken. Von ERNST COHEN, Professor an der Reichs-Universität zu Utrecht. Mit 2 Gravüren und 90 Abbildungen. Grosse Männer, Studien zur Biologie des Genies. Herausgegeben von WILHELM OSTWALD. Band 3. Leipzig: Akademische Verlagsgesellschaft m. b. H. 1912. S. XV + 638. Preis: geh., M. 14.75; geb., M. 16.

A large number of biographical sketches of van't Hoff have recently appeared. Most of these were *in memoriam* notices and very, very brief and incomplete. When such a man appears in any branch of science it is well that he should have a competent and willing biographer, since the perusing of such a life often stirs the instinct of young men and women to do something themselves.

Van't Hoff has been very fortunate in this respect, in that his assistant and friend—Cohen—has both a skilful and willing pen, and this work is literally a labor of love.

The book deals with the life of van't Hoff in periods. The first period has to do with his youth, the second with his student life, and his "Wanderjahre." The third period discusses his return to Utrecht, and his earlier investigations, especially in the field of stereochemistry. Letters to van't Hoff during this period show the reception of this work on the part of a number of the leading chemists.

Van't Hoff's Amsterdam period is treated in five sections. The period from 1877 to 1884 marks the beginning of his work in this important university. The second period, 1884–1885, has to do especially with the publication of his "Etudes de dynamique chimique."

The third period, 1885–1887, was the one in which the relation between gas pressure and osmotic pressure was pointed out, and to account for certain exceptions to this relation, the theory of electrolytic dissociation was proposed by Arrhenius.

The fourth Amsterdam period (1887–1894) was characterized by great development in the field of general chemistry, being largely applications of the generalizations already reached by van't Hoff. The last Amsterdam period, 1894–1896, was not marked by the same activity as the earlier.

In 1896 van't Hoff was called to the University of Berlin and accepted the call. His work while in Berlin, especially in connection with the Stassfurth salt deposits, is too well known to call for special comment in this brief review.

The long and close relation of Cohen to van't Hoff, his admiration for his teacher and colleague, and the literary skill

of the author of this book in presenting things in an attractive form, make this an authoritative and very readable treatise on the life and work of one of the truly great men of science of his day—of one of the very greatest chemists of all time. H. C. J.

DIE EXISTENZ DER MOLEKÜLE. Experimentelle Studien von THE. SVEDBERG, Professor an der Universität Upsala. Mit 4 Tafeln und 76 Abbildungen im Text. Leipzig: Akademische Verlagsgesellschaft. S. 243. Preis: brosch., M. 12.00; gebunden, M. 13.20.

As the author says in his preface, this book deals chiefly with his own experiments, the work of other investigators being alluded to only as it has a bearing upon his own. He seeks to obtain experimental evidence of the existence of molecules as discrete entities.

The first part of the book is made up of a very full account of a long series of experiments on the colors of colloidal and true solutions, the larger part of the matter consisting of numerical tables and series of observations. In the opinion of the reviewer these could have been left out, or at least expressed in graphical form only, as they are bulky and not very readable.

The author reasons as follows: If a colloidal solution, in which the material can be seen with the microscope to exist in a state of very fine subdivision, shows certain properties, such as color produced by absorption, and these properties pass by gradual transitions to the properties shown by true solutions, *as the size of the particles is reduced* by appropriate means, we have strong evidence that even in the true solutions the dissolved matter is present in a state of fine subdivision (molecules) and not uniformly distributed (i. e., continuous). He investigates the phenomenon by a colorimetric method and also with the spectrophotometer, studying colloidal solutions of gold, ferric oxide, arsenous sulphide, selenium, indigo, aniline blue, indophenol and azobenzene.

In some cases the absorption increases as the size of the particles is diminished, reaching its maximum value in the true solution. In other cases, azobenzene, for example, the reverse is true.

In the opinion of the reviewer, these experiments do not furnish much evidence for the existence of molecules. The action of very small bodies upon light waves is so dependent upon their size, and so little understood, that experiments of this nature can be interpreted only with difficulty. Granular deposits of metallic sodium and potassium formed by heating the metals in exhausted bulbs show all colors of the

rainbow in transmitted light, the color appearing to depend upon the size of the small metal particles. Granular deposits of selenium and some of the aniline dyes behave in the same way.

Professor Svedberg's argument that if the properties of colloidal solution in which the microscope reveals small particles can be made to pass gradually to the properties of a true solution, by reducing the size of the particles, then the true solution must contain still smaller particles (i. e., molecules), does not appear to be quite free from objection. It seems conceivable that the same might be true if, in solutions, the substance dissolved was continuous. In the second part of the book the author deals with diffusion phenomena, and here his arguments are much more convincing. He compares the rates at which substances in the colloidal form diffuse into pure water, as dependent upon the sizes of the particles, and compares them with the rate at which the dissolved substance diffuses. If the same law is followed in each case, it is a strong argument for the existence of molecules. His investigations of the sizes of molecules of certain organic compounds by this method is especially interesting.

By the study of diffusion he calculates the sizes of the particles in colloidal solutions, and compares them with the sizes observed with the ultramicroscope. The diffusion experiments certainly give strong support to the molecular theory.

The author makes no mention of the recent work of van Calcar and Lobry de Bruyn, who showed that centrifugal force alters the concentration of a solution, and may even, in the case of a saturated solution, cause crystallization along the periphery of the centrifuge. Such a separation could scarcely occur if the specific gravity were constant in every infinitesimal element of volume, as would be the case if the dissolved substance were continuous.

Absorption and diffusion belong to the class of multimolecular phenomena, as the author calls them, since their study is associated with the observation of effects produced by large numbers of molecules. Of greater extent is the paucimolecular class which is next considered, for here we deal with effects produced by a few molecules or in some cases by a single molecule.

The author draws attention to the following phenomena, all of which, with the exception of the first, have been discovered since 1903:

1. The "Brownian" movement of small particles in suspension, which is now definitely ascribed to the circumstance that

for very small particles the resultant force of the molecular impacts from all sides is not zero. Particles of smoke, suspended in air, are shown by the microscope to be in violent agitation, as the result of the molecular bombardment to which they are subjected. In a gas, in which the molecules are moving according to the kinetic theory, there will be moments at which a given minute volume will contain more molecules than at others, in other words, the density of the gas will vary from point to point. If a smoke particle lies between a region of high and a region of low density, it will move towards the latter, as a result of the greater pressure exerted on one side. This, of course, amounts to the statement that the resultant force of the impacts is not zero, given below.

2. The "scintillation" of zinc sulphide produced by the impacts of α particles from radium (Crookes).

3. The ionization of a gas produced by the passage of a single α particle through it, discovered by Rutherford.

4. The photographic records of the impacts of single α particles upon photographic plates (Kinoshita).

5. Wilson's experiments for showing the tracks of single α particles by condensing water vapor on the ions formed in their paths.

6. The variations in the ionization current observed by Meyer[1] explained by departures from the "mean free path" of the kinetic theory.

7. The observations of Svedberg on the spontaneous concentration variations in radioactive solutions and gases.

Of the above phenomena the first and the last are the only ones to which the author devotes much space. The description of his experiments on the Brownian movement requires two hundred pages, nearly one-half of which are devoted to numerical tables of observations.

The spontaneous concentration variations of colloids are investigated and the movements of the individual particles studied by photographic and other methods, and the results compared with the theories developed by Einstein and v. Smoluchowski. The effects increase as the size of the particles is diminished, and are in perfect accord with the molecular kinetic theory.

The last portion of the book is devoted to the spontaneous concentration variations which occur in radioactive solutions and gases (radium emanation, for example).

The solution in the form of a thin film is brought in close proximity to a screen of phosphorescent zinc sulphide under

[1] Physik. Z., **11**, 215 (1910).

the microscope, and the scintillations resulting from the bombardment by α particles observed. In this way the space distribution of what we may term the "exploding" radioactive molecules in the solution can be studied. A similar method is used with the emanation.

We have, as yet, no experimental means of detecting the variations of concentration in solutions except in the case of radioactive substances. There is no doubt but what they occur, in fact they must occur if the molecules of the dissolved substance are moving about, in a manner analogous to the density variations of gases referred to previously.

The book could have been made more interesting by condensation, and by the omission of most of the numerical tables of observations. R. W. W.

ATOMPROZENTE UND GEWICHTSPROZENTE, sowie die Methoden zu ihrer gegenseitigen Umwandlung. Ein metallographischer Beitrag zur graphischen Technik der physikalischen Chemie. Von DIPL.-ING. FRITZ HOFFMANN. Ingenieur der Berndorfer Metallwarenfabrik Arthur Krupp, Berndorf (Nieder-Oesterreich). Halle a. S.: Verlag von Wilhelm Knapp. 1912. pp. 20. Price, M. 1.80.

In the study of the alloys for the purpose of determining the presence or absence of definite metallic compounds, it is necessary to know the atomic relations of the elements rather than the weight relations. The author has illustrated three methods of changing weight percentages into atomic percentages: (1) A mathematical method. (2) A combined mathematical and graphic method. (3) A purely graphical method. The graphical methods are explained by numerous diagrams.

The monograph should be of value to anyone working in the field of heterogeneous equilibria, especially if three or more components are involved. ROBERT S. WILLIAMS

DIE ELEKTROCHEMISCHE INDUSTRIE FRANKREICHS. Von M. R. PITAVAL, Ingénieur-Directeur, ins Deutsche übertragen von DR. MAX HUTH, Chemiker der Siemens & Halske A.-G., Berlin. Mit 35 in dem Text gedruckten Abbildungen. Monographien über angewandte Elektrochemie. Herausgegeben von VIKTOR ENGELHARDT. XLII Band. Halle a. S.: Druck and Verlag von Wilhelm Knapp. 1912. pp. viii + 140. Price, M. 9.00.

The French author, well known through his reviews upon the progress in the electrochemical industries of France, has brought together, in compact form, their present status. The chlorine industry receives 12 pages, calcium carbide 12, fixation of atmospheric nitrogen 17, and the metals 68. Of the last, the aluminium industry alone has 15 pages, copper 10, and steel 27.

The book has the good points of most French technical pub-

lications, logical arrangement and clear exposition of the subject; it has also the unwelcome feature of not giving the sources whence the information has been derived. The reader has no means of knowing how much reliance can be placed upon the several statements; he is forced to look for other sources and make comparisons before he can accept the figures.

That the publication of the book is one of the well-known collection of monographs upon Allied Electrochemistry edited by V. Engelhardt is in its favor; it shows that European electrochemists, familiar with the work in France, think favorably of the treatment of the subject. The translator does not seem to appear familiar with German metallurgical terms, e. g., on page 88 "Matten" is a germanization of the French "mattes;" the corresponding German word is "Steine."

H. O. HOFMAN

ABSTRACT-BULLETIN OF THE PHYSICAL LABORATORY OF THE NATIONAL ELECTRIC LAMP ASSOCIATION, Cleveland, Ohio. EDWARD P. HYDE, Director. January, 1913. Vol. 1, No. 1. Cleveland: The Physical Laboratory of the National Electric Lamp Association. 1913. pp. viii + 127.

The purpose of this publication is best expressed in the words of the Director of the Laboratory:

"The Physical Laboratory of the National Electric Lamp Association was organized in the autumn of 1908 for the development of those branches of science with which the art of lighting is closely associated. Up to the present time, sections in physics, physiology and psychology have been organized.

"The results of the investigations carried out in this laboratory have been presented before the various scientific and technical societies of the United States, and have been published in the proceedings of those societies and in the recognized scientific and technical journals of this country and Europe. It has seemed unwise to restrict the publication of these investigations to a new journal issued by the Laboratory, or to reproduce the published papers in full in such a Laboratory bulletin. And yet it has seemed advisable that the complete work of the laboratory should be collected in such a way as to render it available to all who may be interested.

"To this end the present *Abstract-Bulletin* is being published and distributed. This *Abstract-Bulletin* contains an abstract of every research carried out in the laboratory from its inception to the summer of 1912. The abstracts, written by the authors of the original papers, are fully illustrated with photographs and drawings, in the hope that to all, except those

specially interested in the details of the investigation, they may be satisfactory substitutes of the original papers.

"Subsequent numbers of the *Abstract-Bulletin* will be issued as the further accumulation of published investigations may warrant."

To the reviewer this seems a step in the right direction. Taking the field of chemistry alone, the literature has grown to such an enormous bulk and is yearly increasing to such an extent, the multiplicity of journals is such, that no one, however narrow his field, can hope to be able even to glance through all the journals which may contain articles of value to him, to say nothing of subscribing to them, and it is taxing even the best-equipped libraries to keep up with the rising flood. The necessity of abstract journals is therefore recognized by every one. And who is better qualified to prepare an abstract than the author of the original article himself? Of course, the tendency in such a case is to make the abstract too long, but this ought to be easily overcome by judicious editing. This plan of abstracts by authors would ensure better and more accurate work, would relieve the various societies already publishing abstract journals of great expense and would allow many men now giving much of their time to abstracting to apply their energies to more productive work. But the question arises, How many abstract journals are we to have? Every duplication is, of course, a waste of time, money and effort. Until the millenium of a universal language is reached, it will probably continue to be necessary to have an abstract journal in, say, English, German, French and possibly Italian, for a large majority of those to whom an abstract journal is most useful, viz., those not having access to a large library, have neither the time nor opportunity to master another than their native language. But why could not an International Association of Chemical Journals be formed which should limit the publication of abstract journals by its members to one in each language, and require that all original papers submitted for publication be accompanied by a brief abstract, a copy of which could be sent to each of the four or five abstract journals? The cost of translation of such abstracts would be negligible as compared with the present system, errors would be reduced to a minimum, the abstracts could be published immediately after the appearance of the original and every reader could get a journal which was published in the language most useful to him.

C. A. R.

EXPLOSIVES. A Synoptic and Critical Treatment of the Literature of the Subject as Gathered from Various Sources. By DR. H. BRUNSWIG, Translated and Annotated by CHARLES E. MUNROE, PH.D., LL.D., and ALTON L. KIBLER, M.S., PH.D., George Washington University. New York: John Wiley & Sons; London: Chapman & Hall, Ltd. 1912. pp. xv + 350.

This book is a notable contribution to the literature of explosives; its scope can hardly be better stated than in the following extracts from its preface: "The indefatigable labor of decades in the manufacture and use of explosives has yielded rich experimental material which is still waiting a thorough working over and coördination in accordance with scientific laws. * * * The development of our knowledge of explosive processes forces us more and more into the narrow field of an exact chemistry of explosives, or, in other words, a physical-chemical science dealing with the velocities of chemical reactions and chemical equilibria at very high temperatures and pressures. * * * It seems a worthy task to gather together the facts recorded in the literature of explosives, arrange them in accordance with the physical-chemical views, and take a survey of the present status of the chemistry of explosives and its most important aims. * * * Theoretical-mathematical discussions have been carefully omitted in the following pages. * * * We have made use of only such experimental facts as are found in the literature within every one's reach."

In accordance with this program the book is divided into two parts, the first considering the conditions governing explosive reactions; the influence of surrounding circumstances on the initial velocity of reactions and of propagation, including temperature, pressure and catalytic influences; the rate of increase and the maximum of the pressure developed; the temperature of explosions; the influence of pressure and temperature on the gases developed by explosive reactions; the velocity and intensity of explosions by influence; and the flame of explosions, especially of interest in connection with fire-damp problems.

The second part of the book treats of the characteristics of particular explosives and of the various modes of igniting them. They are classified according to their uses as propellants or for blasting purposes. For each variety its history, its composition, its preparation and its properties are treated. Nearly one-third of the book is devoted to this branch of the subject, and several tables facilitate the comparison of the different types. Cautions on the handling and, when necessary, on the destruction of explosives are given, with details of some important works accomplished by their

aid. Convenient indices of authors mentioned in the text, and of the many subjects treated, complete the work.

In fine, the book supplies information long needed both by theoretical scientists and by practical technologists. The authors are to be congratulated for supplying a need long felt.

HENRY L. ABBOT

A MANUAL OF CEMENT TESTING, for the Use of Engineers and Students in Colleges and in the Field. By WILLIAM ALLYN RICHARDS, B.S. IN M.E., Instructor in the University of Chicago, and HENRY BRIGGS NORTH, D.Sc., Associate Professor of Chemistry in Rutgers College. Illustrated. New York: D. Van Nostrand & Co. 1912. pp. x + 137. Price, $1.50.

This little book was written as a laboratory guide for students in the engineering courses of our schools and universities and its style and arrangement are extremely elementary. It may, however, prove helpful to inexperienced cement testers in field laboratories when they have not learned the rudiments of the various principles involved. The object claimed for it is to promote greater uniformity in cement testing and the various steps of procedure are explained in detail. It has been compiled from the standard treatises on cement testing and full credit is given at the end of each chapter.

The book is divided into two parts and appendix. The first part describes the methods used in the physical testing of cement and the various aggregates used with it; the second part treats of the chemical analyses of the above and the appendix is a reprint of the standard specifications and uniform methods of testing and analyses as adopted by the principal engineering societies.

The methods for chemical analysis are most too academic for the practical cement chemist but, by following the instructions given, little error will enter into his determinations.

The paper and binding are good, the type large, clear and well spaced. Forty-six illustrations of fair quality are included in the text.

C. N. WILBY

AUSFÜHRUNG QUALITATIVEN ANALYSEN. Von WILHELM BILTZ. Mit 1 Tafel und 13 Figuren im Text. Leipzig: Akademische Verlagsgesellschaft m. b. H. S. xi + 139. Preis: brosch., M. 5.00; geb., M. 6.00.

This little book on Qualitative Analysis differs from most of its predecessors in that its author's purpose has been to show how the constituents of a mixture may be determined as quickly as possible, and with reasonable accuracy, rather than to lay particular stress on the detection of very small quantities or to make the qualitative study of the metals serve as a reason for the introduction of a mass of information

about each element. Nearly one-third of the book is devoted to "Dry Reactions." The author feels that these tests should not be classed as preliminary, to be used or not at the discretion of the analyst, but that they should form an integral part of the scheme and in certain cases should replace the usual wet methods. This part of the book seems to be given undue emphasis from the view point of the general analyst to whom dry reactions cannot be as helpful as they are to the mineralogical chemist. The scheme of wet analysis is about the usual one but contains no equations and very few reasons for the procedure. The characteristic feature of this part of the book is the weight which the author places on analytical style as illustrated in his frequent paragraphs on "methods of work." The last page is devoted to "Analytical Don'ts," the free translation of one of which well illustrates the author's attitude throughout. "Don't take the time and trouble to separate iron from manganese by a careless application of the quantitative basic acetate method when each may be detected in the presence of the other by a simple color reaction."

The book has many valuable suggestions and for the mineral chemist is well suited to the purpose for which it was written. It is not suitable for a teaching book unless used as a laboratory manual in connection with one of the larger works on Qualitative Analysis. R. S. WILLIAMS

GRUNDRISS DER ANORGANISCHEN CHEMIE. Von PROF. CARL OPPENHEIMER. VII Auflage. Leipzig: Verlag von GEORG THIEME. 1912. pp. 196. Price, M. 3.50.

This book, which is intended for the use of medical students, pharmacists, architects, etc., contains a considerable amount of information in a very condensed form. It may be of use to one who wishes to learn enough to pass an examination, but is of little value to one who wishes to really know something of the science of chemistry. J. E. G.

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Persons interested should write to the United States Civil Service Commission, Washington, D. C. Letters of inquiry must be received by the Commission prior to May 15, 1913. Efforts will be made to reach a decision on this appointment by June 1, 1913.

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